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BULGARIAN JOURNAL OF SOIL SCIENCE®

CONTENTS

VOLUME : 3

ISSUE : 2

PAGES : 79 - 158

Soil Genesis and Formation

- 1 Some Features of Cambisols Soil-forming Process from Training and Experimental Forest Range (TEFR) „Petrohan” Region. 81 - 89
Kameliya Petrova

Soil profile diagnostic

- 2 Profile Distribution of Physical and Chemical Soil Properties in Izombe, Rainforest Zone of Nigeria. 90 - 103
Donald Nweze Osujieke, Pedro Ezemon Imadojemu, Michael Akpan Okon, Obinna Marcellinus Okeke

Soil Chemistry and Agroecology

- 3 Sulphur Balance in Agroecosystem. 104 - 118
Marija Galic, Milan Mesic, Aleksandra Percin, Ivana Sestak, Zeljka Zgorelec

Soil Microbiology

- 4 Soil Enzymes Assessment around Amega Cement Factory in Nigeria. 119 - 133
Oluseye Olalekan Oludoye, Lanrewaju Amos Ogunyebi

Land Evaluation

- 5 Opportunities for Growing Lavender in Areas Facing Natural Constraints Exemplified by the Borika Village, Bulgaria. 134 - 142
Zornitsa Mitreva, Veselin Pankov

Soil Productivity and Fertilization

- 6 Changes in Biomass Accumulation and Soil Properties after Fertilization of Ryegrass. 143 - 149
Vania Kachova

International Meeting

- 7 “Payment for Ecosystem Services-Forest for Water” (CA15206 PESFOR) 150 - 154
Mariyana Lyubenova, Gregory Valatin

Instructions for Authors 155 - 158



Some Features of Cambisols Soil-Forming Process from Training and Experimental Forest Range (TEFR) „Petrohan” Region. Kameliya Petrova



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Abstract:

Dystric/eutric Cambisols diagnostic features from TEFR Petrohan were investigated in the present study, which morphologically corresponded to Podzols. Diagnostic horizons were investigated to establish presence or absence of podsolization process and to classify the soil type according to the modern requirements of WRB, (2006, 2007; 2014). Humus forming process *insitu*, clearly expressed in the A_h horizon, acidification, degradation of clay minerals, formation of *E* horizon, which is clay-poor with increased content of sand, accumulation of Fe and other mobile elements in *Bw* horizon were established. The metamorphic *Bw* horizon had some diagnostic properties, which met these of *spodic* horizon. This horizon is specific for the Podzols. The content of organic carbon in it was less than 0.5 %. Cambisols properties are predominant. It was established that the soil-forming process in the investigated Cambisols is directed to podsolization process.

Key words: Cambisols, Podzols, org.C, *albic*, *spodic* diagnostic horizon

Introduction

Dystric/eutric Cambisols are significant for the forestry in Bulgaria. Depending on the combination of the main soil forming factors, in some of them are established specific processes. For example, one of them is the podsolization process that creates conditions for the formation of a new soil type called Podzols.

Some of the first sources of information for the Podzols are mentioned in Russian literature in the 1950s (Williams, 1949, Garkusha, 1951, Vilenskii, 1954, Russel, 1955, Alexandrova et al., 1958). In the following years, a number of authors (Petersen, 1976, Mokama and Buurman, 1980; Anderson et al., 1982; Petersen, 1984; Buurman, 1984; Lundström et al., 2000) studied their genesis, chemical, mineral composition and key features.

According to the World Reference Base for Soil Resources (WRB, 2006, 2007) and the International Union of Soil Sciences (IUSS) Working Group WRB, 2014 Podzols covers 485 million ha worldwide, mainly in the temperate and boreal zone of the northern hemisphere. They occupy vast territories in Scandinavia, Northwest Russia and Canada.

The first information in Bulgaria about these soils is given by Boyadzhiev in 1967. It is known that they are distributed mainly in the middle and high mountain areas. They are formed under the influence of coniferous and mixed forests, humid, cold climates and silicate rocks. According to Achkov's studies (1980, 1981), the soils that correspond to in the country are Cambisols. They can evolve at a certain stage of their development into Podzols. This

statement is confirmed by other authors (Dialo, 1995; Teoharov et al., 1995). Cambisols can change and form a *spodic* diagnostic horizon, which is specific for the Podzols. In them it is formed under the influence of climate change and the dominant vegetation, anthropogenic impact, etc., which alter the processes of decomposition of the litter and lead to the accelerated formation of water-soluble organic acids (Lundström et al., 2000; Sauer et al., 2007).

In Bulgaria a podzolization process of Umbrisols was described by Achkov (1980) in the high parts of the Rila mountains - 2485 m and an initial stage of podzolization process at an altitude of 1460 m - 1470 m also in Rila (1981). The presence of a typical *spodic* diagnostic horizon is mentioned by Dialo (1995), at an altitude of 1450 m in Pirin mountains. According to Dialo (1995), these soils are still not well described in the country, but they are a separate taxonomic unit and should find a place in the soil classification of Bulgaria. Boyadjiev has also mentioned the Podzols (1994a, 1994b), when he has established a correlation between the American Taxonomic System and that of the revised FAO-UNESCO-ISRIC legend with the Basic Soil Classification in Bulgaria. It is clear that the correlation is completely possible and necessary.

According to unpublished data of Yordanov (1985) on the territory of the TEFR Petrohan there is a Podzols with clear morphological features. For this soil, no parameters have been studied so far that characterize the elementary soil-forming processes and diagnostic features to prove the *albic* and *spodic* horizons necessary for the definition of a Podzols, according to WRB requirements (2006, 2007 and 2014). The aim of the present study is to investigate the diagnostic features of Cambisols from the territory of the TEFR Petrohan, which morphologically corresponds to Podzols, to determine the diagnostic horizons, to establish the presence or absence of podzolization process and to classify the soil type according to WRB's modern requirements (2006, 2007, 2014).

Materials and Methods

The investigated soil is located at 1400 m altitude at the southern exposure. It has a depth of 30 cm and more. The soil-forming rock is granite. The litter is 1 cm, torn by grass and shrubs mainly covered by blackberry (*Vaccinium myrtillus* L.) and blueberry (*Vaccinium uliginosum* L.). When plotting the soil profile, morphological features different of these of Cambisols and typical for Podzols were established. The strongest impression was the colour change of separate horizons that point to the presence of *albic* and *spodic* diagnostic horizons. In the soil profile are defined AturfAEBC horizons by morphological features.

Parameters that characterize diagnostic *albic* and *spodic* horizons are investigated: colour by horizons (Munsell scale); Texture - Modified Kachinski method (dispersion with sodium pyrophosphate); pH (CaCl₂) - ISO 10390; pH (H₂O) - ISO 10390; Organic carbon - Modified Turin's method (Kononova, 1963; Filcheva E., S. Tsadilas, 2002); exchange cations - ISO 11260 & ISO 14254, 0.1 M / l BaCl₂ solution and AAS Perkin Elmer 5000; exchangeable acidity - ISO 11260 & ISO 14254 (extract with 0.1 mol / l BaCl₂ solution to equilibrium desorption and titration with 0.05 mol / l NaOH); Fe content - by decomposition with Aqua regia and Flame AAS (ISO 11466) Perkin Elmer 5000; cation exchange capacity - determined as a sum of the basic cations and the exchangeable acidity.

Results and Discussion

Studies on the *E* albic diagnostic horizon showed full compliance with WRB requirements (2006, 2007 and 2014). It laid directly under the humus-accumulative horizon. The distinctness between them was clear. The topography between the *E* and the *B* horizon was wavy with slightly albeluvic features. The soil's colour in the *E* horizon was bright - 10 YR 6/1 (when dry). It met the requirement for a value of less than 7 and a chroma of less than 3 WRB, (2006, 2007, 2014) (Table 1).

Table 1. Soil colour by horizons (Munsell scale)

Horizon	Soil Depth (cm)	Distinctness	Colour
O	1-0	-	-
A_h	0-7	clear	10 YR 3/2
A	7-14	clear	10 YR 3/3
E	14-20	clear	10 YR 6/1
B_w	20-30	clear	7.5 YR 4/4
C	30 -↓	clear	10 YR 6/3



Photo 1. Soil Profile

On the field, the *B_w* horizon was determined as a *spodic* diagnostic horizon. The requirements of WRB (2006, 2007; 2014) for its definition are: for colour, soil depth, amount of org. C, pH_{H_2O} and absence of a *natric* diagnostic horizon, with a high content of exchangeable Na, and / or Mg.

The study showed that the soil colour in the *B_w* horizon corresponded to the requirements. It was determined as 7.5 YR 4/4 (when moist) and met the requirement for hue 7.5YR, value 5 or less and chroma 4 or less. It laid directly below the *albic* diagnostic horizon. The soil depth of *B_w* horizon was 10 cm, which met the requirements for *spodic* horizon - minimum 2.5 cm. The pH of the soil solution was - $pH_{H_2O} = 5.2$ and also met the requirements for a *spodic* diagnostic horizon - pH_{H_2O} of less than 5.8 (Table 2).

A disparity with the *spodic* diagnostic horizon requirements of the WRB (2006, 2007; 2014) was established only with respect to the amount of org. C, which was very low and did not exceed the minimum of 0.5% . The result was obtained as an average sample of the entire 10 cm soil depth of the horizon (Figure 1).

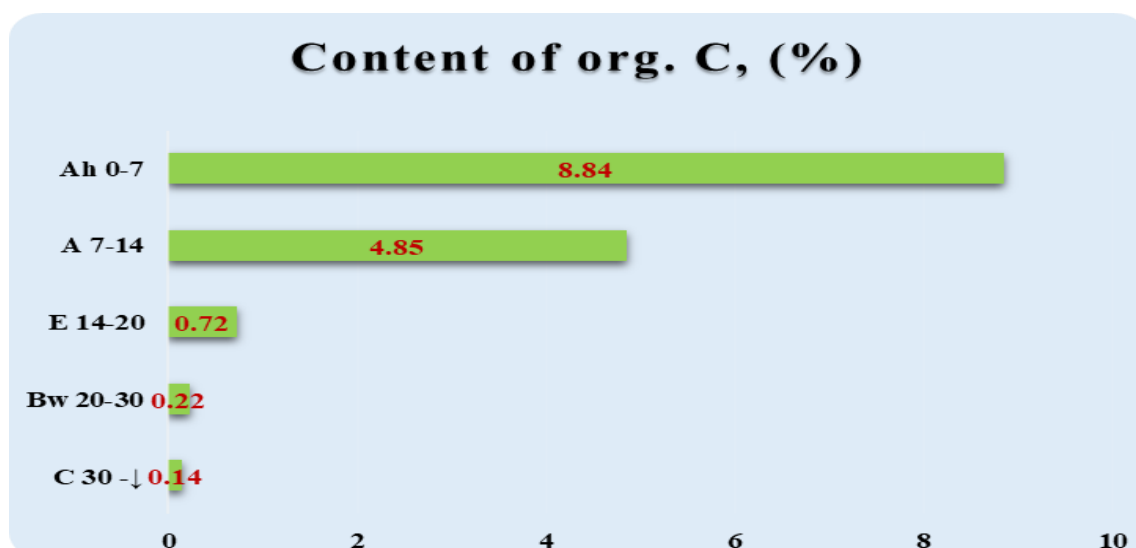


Figure 1. Content of org. C, (%) in the soil profile

In order to trace the distribution of org. C in Bw horizon, it was divided into 4 parts by 2.5 – as the required thickness for *spodic* diagnostic horizon (Figure 2).

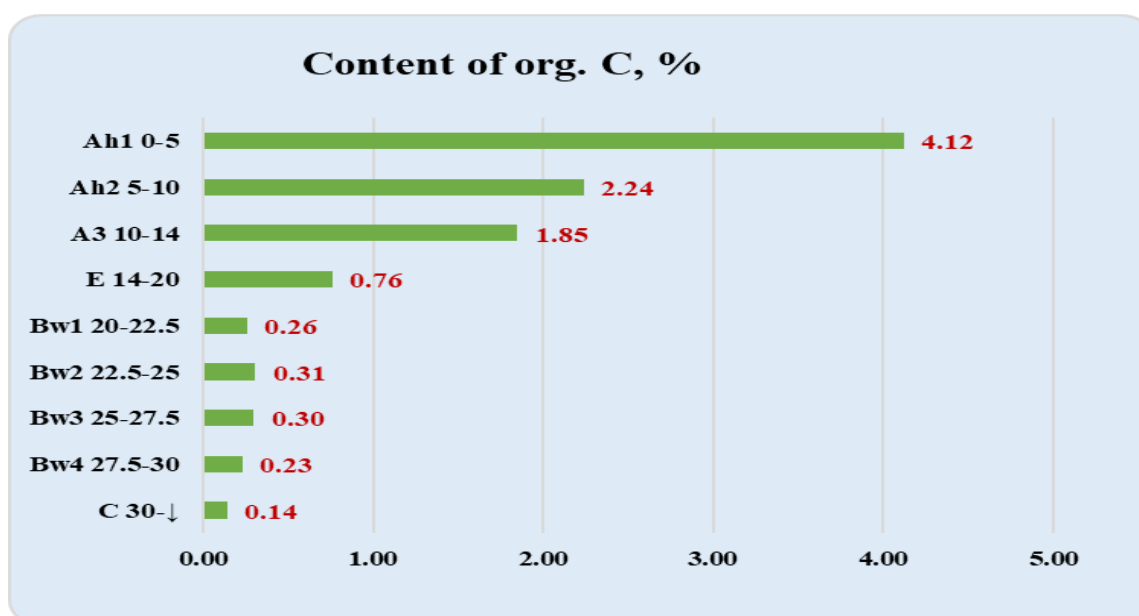


Figure 2. Content of org. C, (%) in the soil profile

It was found that in none of these layers the amount of org. C did not exceed 0.5%, which indicated that it could not be define as a *spodic* diagnostic horizon. The soil was determined as Cambisols. Nevertheless, there were processes, which indicated its future evolution towards podzolization, such as formation of acidic humus, acidification of the soil, destruction of clay minerals and transport of products in soil depth.

A high amount of organic matter was accumulated in the surface soil horizon. The organic matter exceeded 15% in the first part of it (Ah horizon). It should be noted that in the soil depth of the profile its amount decreased almost twice in the lower part of the A horizon, followed by a rapid decrease to E and Bw horizons. This change was due to the removal of organic matter from E horizon in depth. As a reason, high acidity can be noted. Soil response

is an important diagnostic indicator. In the *Ah* horizon it was estimated to be very highly acidic. The soil reaction had the lowest values in it ($\text{pH}_{\text{H}_2\text{O}} = 4.1$). The origin of this acidity was a result of the introduction of free organic acids from the decomposition of the roots that form the *Ah* horizon and partly from the litter. According to some authors (Ganev, 1990) values of $\text{pH}_{\text{H}_2\text{O}}$ below 4.8 are an indicator of the presence of free fulvic acids in the soil. Funakawa et al. (2006) point out that the pH around 4.0 is the critical limit that enhances the mobilization of org. C in the litter and in the surface soil layer. This causes its mobility into the soil depth of the profile in the form of a soluble organic substance.

In the second part of the *A* horizon the value of $\text{pH}_{\text{H}_2\text{O}}$ continued to be very low. This means that there is a removal of soluble organic matter from it. In depth of the soil profile, the $\text{pH}_{\text{H}_2\text{O}}$ values increased slightly, in *E* horizon its values remained within the range of the highly acidic spectrum. The profile distribution of $\text{pH}_{\text{H}_2\text{O}}$ showed the predominance of acidic products from the decomposition of the organic matter over the basic ones - of the weathering processes in the *C* horizon.

The exchangeable acidity values, measured as $\text{pH}_{\text{CaCl}_2}$, showed that the soil buffer capacity was achieved due to Fe oxides dissolved as well as the weathering of secondary clay minerals (Ulrich scale, 1983). This referred to the depth from *Ah* to *E* horizon including. In the horizon, a major buffer process was the exchange of protons with basic cations. The titrimetric determined exchangeable acidity was very high. Its profile distribution is represented in Figure 3 and shows the high degree of acidification in the surface soil horizon, which is rich in humus.

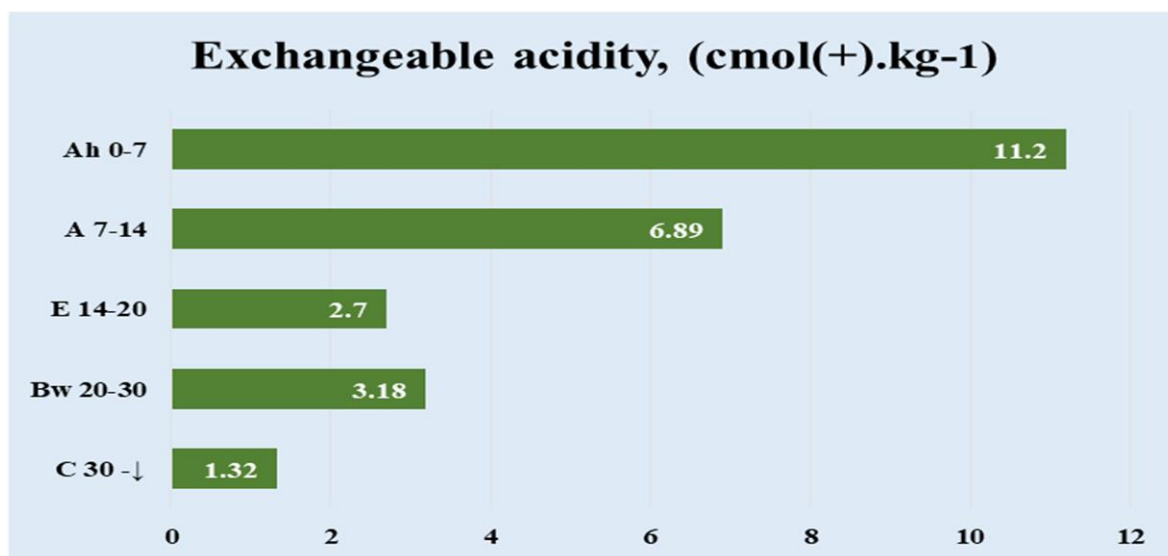


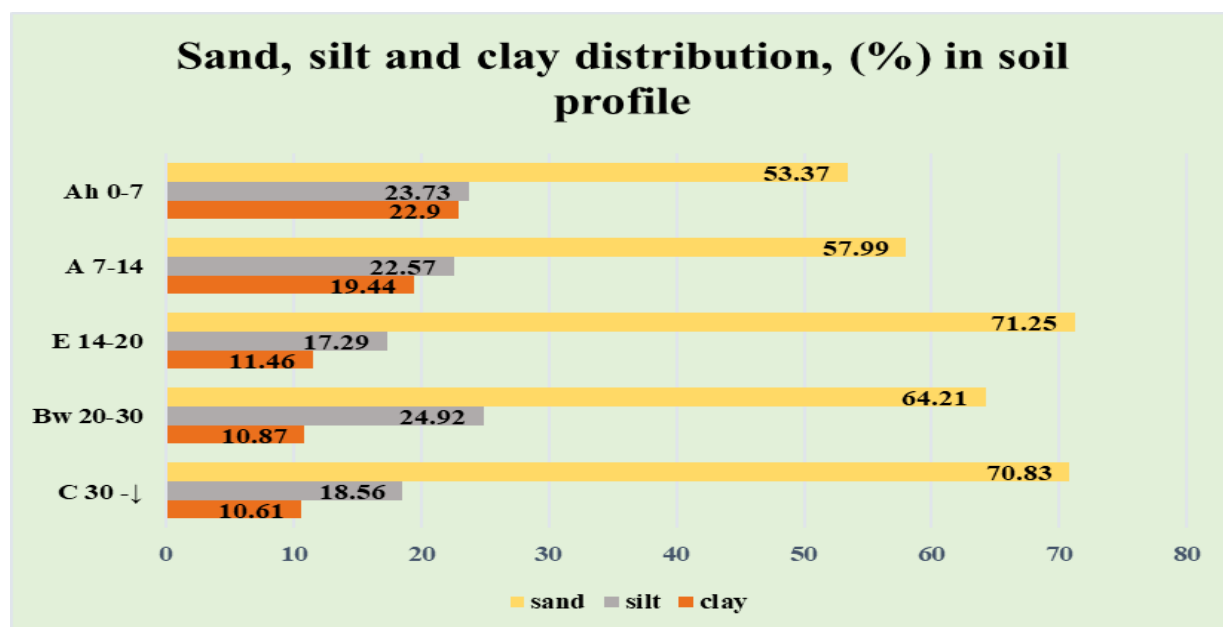
Figure 3. Exchangeable acidity in soil profile

Under the influence of high acidity, the soil was highly leached. Basic cation values were low, with their lowest levels in the *A* horizon. The sum of the basic cations in the *Ah* and *A* horizon was: 1.99 cmol(+).kg⁻¹ and 0.42 cmol(+).kg⁻¹. Cation exchange capacity (CEC) values were highly differentiated between *A*, *E* and *Bw* horizons. In *E* horizon the CEC decreased 2.7 times compared to the *A* horizon. The results of the soil texture supported this assumption (Figure 4).

Table 2. Soil solution reaction, exchangeable cations, cation exchange capacity (*T*) and base saturation (*V*)

Horizons	Soil Depth	pH	pH	Exch. acidity	Exch. Ca	Exch. Mg	Exc h. K	Exch. Na	Exch. Fe	Exc h.Mn	Sum of basic cations	CEC T	BS V
	cm	H ₂ O	CaCl ₂	cmol(+).kg ⁻¹									%
A _h	0-7	4.1	3.3	16.80	1.29	0.45	0.23	0.02	0.27	0.01	1.99	19	11
A	7-14	4.3	3.6	10.33	0.17	0.13	0.11	0.01	0.13	0.00	0.42	11	4
E	14-20	4.7	4.1	4.05	0.17	0.07	0.04	0.02	0.03	0.00	0.30	4	7
B _w	20-30	5.2	4.3	4.76	7.00	1.35	0.03	0.06	0.02	0.01	8.45	13	64
C	30 -↓	5.4	4.3	1.99	6.22	1.59	0.03	0.07	0.02	0.01	7.90	10	80

The profile distribution of the amount of clay showed its rapid decrease from *A* to *E* horizon - 6.7 times. The differences were slightly expressed in the soil depth. *B_w* horizon contained 0.6% less clay than *E* horizon, at the expense of the amount of silt that increased 1.4 times. The amount of sand in the *E* horizon was commensurate with that in the *C* horizon.

**Figure 4.** Sand, silt and clay distribution, (%) in the soil profile

Thus, an *E* horizon was formed, which was clay-poor with an increased amount of sand. It had a coarse texture (sandy loam) than that in the *A_h* horizon (sandy clay loam). It could be assumed that the change of the texture began in the *A* horizon, where due to the loss of clay it was considered as sandy loam. The changes in clay content in the soil profile were accompanied by changes in cation exchange capacity. In *E* horizon CEC decreased rapidly - 2.7 times compared to *A* horizon and 3.2 times compared to *B_w* horizon. This was due to the loss of colloidal particles - organic (Figure 2) and mineral (Figure 4). A podzolization process occurred in the soil.

Some features of podzolization process were also shown by the Fe distribution. It was found to accumulate in *B_w* horizon, where its values reached 39 144 mg/kg (Figure 5).

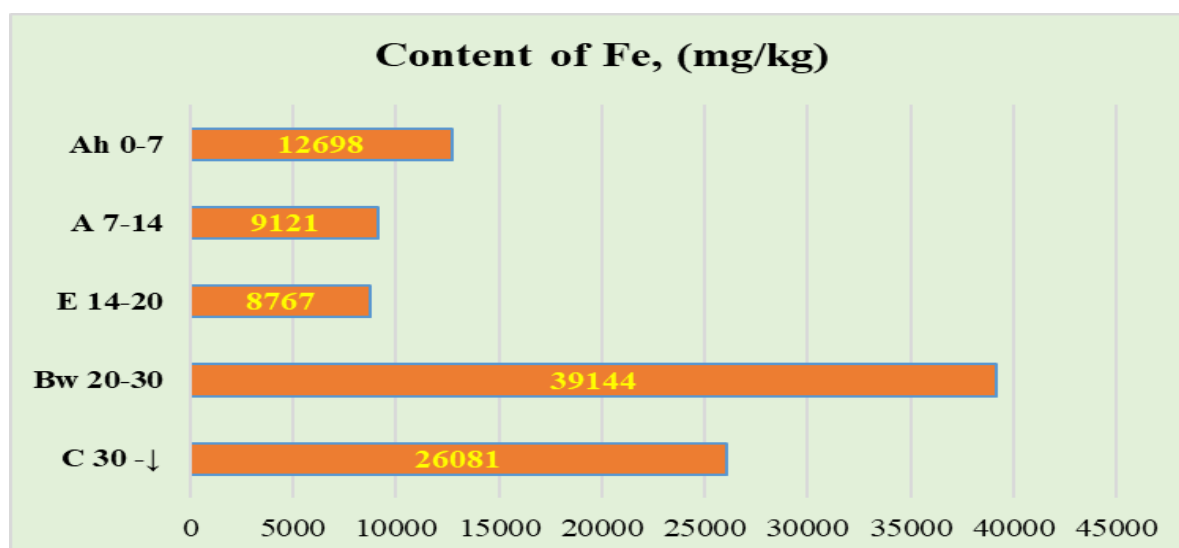


Figure 5. Content of Fe, (mg/kg) in the soil profile

Conclusion

The analysis and assessment of the diagnostic features of the investigated soil did not prove the presence of a *spodic* diagnostic horizon, which did not allow the definition of Podzols. Processes such as: accumulation of acidic humus insitu, removal of org. C, acidification and loss of silicate clay, degradation clearly expressed by the accumulation of Fe in *Bw* horizon, were established. The evolution of Cambisols is related to a complex of specific processes, whose direction is pointed towards podzolization.

Acknowledgments

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2. The current survey was performed in the framework of the project FF -P08 „Qualifier investigation for soil classification update of TEFR Petrohan“ funded by University of forestry.

References

- Achkov, N., 1980. Some features of soil forming in the alpine area of Rila mountains. Soil science and agrochemistry, №4, year XV, vol.XV.78-85. (in Bulgarian).
- Achkov, N., 1981. Specification of the characteristics of soils distributed in the area of Cambisols in Rila mountains. Soil science and agrochemistry, №4, year XVI, vol.XVI.62-70. (in Bulgarian).
- Aleksandrova, L.N., I.N. Antipov-Karataev, I.F. Garkusha, K.P. Gorshenin and C.C. Sobolev, 1958. Soil science. State Publishing House of Agricultural Literature. Moscow.429. (in Russian).
- Anderson, H.A., M.L. Berrow, V.C. Farmer, A. Hepburn, J.D. Russel and A.D. Walker, 1982. A reassessment of podzol formation processes. Journal of Soil Science 33 125-136.

- Boyadzhiev, T., 1967. Contribution to the knowledge of the soils of Bulgaria. Thesis. University of Gent. (in Bulgarian).
- Boyadzhiev, T., 1994a. Soil map of Bulgaria according to the American taxonomic system. Soil science, agrochemistry and ecology. Vol XXIX. 4-6. Sofia.43. (in Bulgarian).
- Boyadzhiev, T., 1994b. Soil map of Bulgaria according to FAO-UNESCO-ISRIC. Soil Science, Agrochemistry and Ecology. Vol XXIX. 4-6. Sofia.52. (in Bulgarian).
- Buurman, P., 1984. Podzols. Van Nostrand Reinhold Soil Science Series. 450pp. New York.
- Dialo, A., 1995. Major genetic processes in soils from some hilly-mountainous territories of southwestern Bulgaria. Thesis. NISSA "N. Pushkarov ".133. (in Bulgarian).
- Filcheva E. and C. Tsadilas, 2002. Influence of Clinoptilolite and Compost on Soil Properties. Communication of Soil Science and Plant Analysis. 33, 3&4, 595-607.
- Funakawa, Sh., K Fujii, A. Kadono and T. Kosaki, 2006. Significance of Soil Acidity to Sequester Organic Carbon in Forest Soils.8-th World Congress of Soil Science. July 9-15, 2006 - Philadelphia, Pennsylvania, USA.
- Ganev, St., 1990. Modern soil chemistry. Science and art. Sofia. 371. (in Bulgarian).
- Garkusha, I.F., 1951. Soil science. State publishing house of agricultural literature. Leningrad.431. (in Russian).
- IUSS Working Group WRB, 2014. World reference base for soil resources 2014. International soil classification system for naming soils and creating legends for soil maps World Soil Resources Reports no. 106. FAO, Rome.
- Kononova, M., 1963. Organic soil. Its nature, properties and methods of study. Academy of Sciences of the USSR, Moscow.314. (in Russian).
- Lundström, U.S., N. van Breemen and N. Bain, 2000. The podsolization process: A review. Geoderma 94:91-107.
- Mokma, D.L. and P.Buurman, 1980.Podzols and Podzolization in temperate regions. ISM Monograph 1. 126 pp.International Soil Museum. Wageningen. The Netherlands.
- Petersen, L., 1976. Podzols and podsolization.Thesis. Forlag Copenhagen.293 pp.
- Petersen, L., 1984. The podzol concept: 12-20p. In P. Buurman (ed.) Podzols. Van Nostrand Reinhold Co. New York.
- Russell, E., 1955. Soil conditions and plant growth. Publishing foreign literature. Moscow.623. (In Russian).
- Sauer, D., H. Sponagel, M. Sommer, L. Giani, R. Jahn and K. Stahr, 2007. Podzol: Soil of the Year 2007. A review on its genesis, occurrence, and functions. Journal of Plant nutrition and Soil Science.Volume 170. Issue 5.581-597.
- Teoharov M., E. Filcheva and A. Dialo, 1995. Humus-forming processes in soils from the hilly-mountainous part of the Southwestern Pirin and its foothills. Collection of scientific papers "Jubilee scientific conference 125 years BAS and 65 years Institute for forests - September 1994", BAS, pp. 183-188. (in Bulgarian).
- Ulrich, B., 1983. Soil Acidity and its Relations to Acid Deposition. In: Effects on accumulation of Air Pollution on Forest Ecosystems. Reidel, Boston. S. 1–29.
- Vilenskii, D.G., 1954. Soil science. Moscow.456. (in Russian).
- Williams, V., 1949. Agriculture with the basics of soil science. State Publishing House of Agricultural Literature. Moscow .471. (in Russian).

World reference base for soil resources (WRB) 2006. World Soil Resources Reports No. 103. FAO, Rome.

World reference base for soil resources (WRB) 2007. World Soil Resources Reports No. 103. FAO, Rome (1st update).



Profile Distribution of Physical and Chemical Soil Properties in Izombe, Rainforest Zone of Nigeria.

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Abstract:

The assessment of the distribution of soil physico-chemical properties facilitates the use of proper soil management practices. Hence, the study was conducted in Izombe rainforest of Nigeria to ascertain the profile distribution of physical and chemical soil properties. Samples were collected from two profile pits base on horizon differentiation for laboratory analyses using standard procedures. Data generated were analyzed statistically using coefficient of variation and correlation. The result indicated that sand recorded 760 g kg^{-1} in pedon 1, 730.20 g kg^{-1} in pedon 2 and was predominant in the soil with higher amount at the surface horizon while clay and silt increased down the pedons. Bulk density ranges from $1.14 - 1.79 \text{ g cm}^{-3}$. The AB horizon was the least acidic of the pedons. Most soil chemical properties decreased down the profile. Sand and pH had low variation ($\geq 4.80 \% \leq 12.60 \%$) while silt, organic carbon, total nitrogen had high variation ($\geq 41.52 \% \leq 79.58 \%$) among the horizons. Fe, Mn and Zn had moderate to high variation among the horizons. Clay correlated negatively and highly significantly ($r = -0.829$, $r = -0.883$, $p = 0.01$) available phosphorus and Fe. Clay also had a positive significant correlation ($r = 0.665$, $r = 0.641$, $p = 0.05$) with bulk density and base saturation. pH had a significant negative relationship ($r = -0.708$, $p = 0.05$) with base saturation while cation exchange capacity had a highly significant positive correlation ($r = 0.877$, $p = 0.01$) with Pb. Fe had a negative and highly significant relationship ($r = -0.838$, $p = 0.01$) with Zn. The result indicated that most mineral element are domiciled in the A horizon and such demand proper management practices for soil nutrients sustainability.

Keywords: distribution, horizon, rainforest, profile pit, soil properties, variation.

Introduction

A vertical cross section through the pedosphere shows varying degree of changes taking place at both surface horizon and subsurface horizons. These changes influence the utilization of these soils for agronomic, engineering, environmental and aesthetic uses. Variation in soil horizons exists at many scales with different dominant controlling factors. Parent material, climate, and geological history are major factors affecting the distribution of soil properties at

continental scale (Akamigbo and Asadu, 1983). Understanding the vertical distribution of soil properties along profile depths could help to predict the proneness of such soils to degradation. Knowledge of their variability is essential in applying location-specific land management interventions (Onweremadu *et al.*, 2015). Soil properties differ among soil profile horizons due to transport and storage of water and nutrient across and within the soil profile. Researchers (Oku *et al.*, 2010) reported that soil pH increased with depth and it is least variable, irrespective of depth. They also found variability of organic matter, total nitrogen, available phosphorus, and CEC to increase with depth and ranged between moderate and high.

Soil is likely to show great variability in their physical, chemical, biological and mineralogical properties because the soil is a heterogeneous unit. Knowledge of variability of soil properties is very indispensable as this determine the productivity and usage of the area. A study of the variability trends of soils is essential in order to highlight the soil potentials and enhance their management and productivity (Mahdi and Mark, 2006; Arnold, 1996). Ogunkunle (1993), working on the Alfisols of southwestern Nigeria, observed that soil pH was the least variable (low variability) property, irrespective of depth. Accordingly, horizons may differ in organic matter content, structure, texture, pH, base saturation, cation exchange capacity (CEC) and bulk density as well as many other soil physical and chemical properties. The rate of soil variation brings about rate of degradation from one location to another due to the composition of soils of the area. There is need to maintain the soil ecosystem through efficient land/soil management practices that will promote food security, soil nutrient balance and sustainable environment. Hence, the work is aimed to assess horizon variations in selected physical and chemical properties of Izombe soils.

LEGEND	
	Study Area
	Inter State Road
	Intra State Road

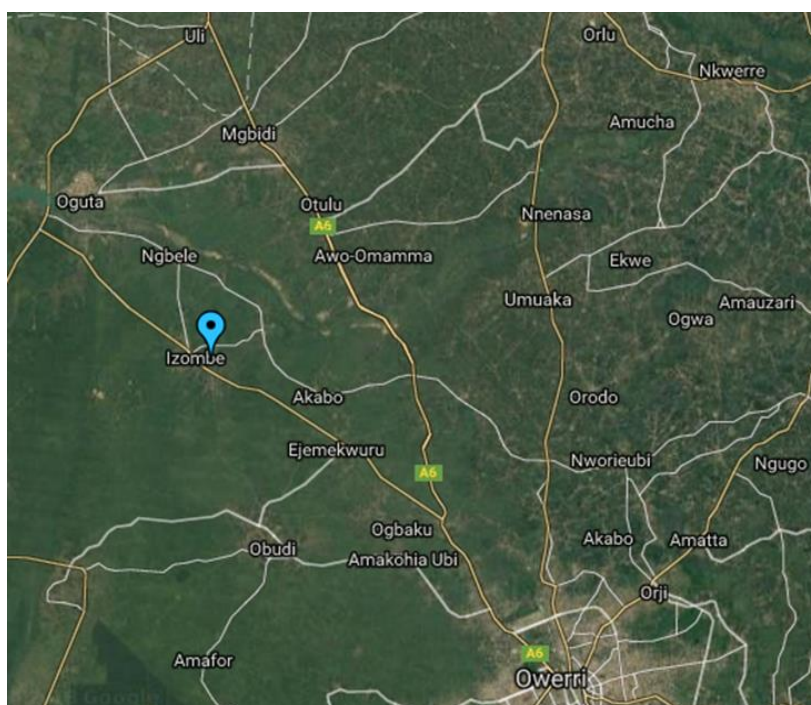


Fig. 1. Location map of the study area (Google Imagery, 2018)

Materials and Methods

Study area

The study area as shown in fig 1 is Izombe in Oguta Local Government Area in Imo state south-east, Nigeria. It lies between latitude 5° 12' and 5° 56' N and longitude 6° 38' and 7° 25' E. The annual rainfall ranges from 2500 mm to 3000 mm with mean temperature of 28 °C (NIMET, 2015). The original vegetation of the study area is the modified tropical rainforest which has been altered by human activities. The greater part of the area now is conserved with trees, shrubs, legumes. The geology of the area consists of alluvium which is marine deltaic deposits (Lekwa, 1985).

Field study and sample collection

A reconnaissance study was carried out on the study areas. Subsequently, free survey technique was used to sink two (2) soil profile pits in the study area. Samples were collected following the guideline of FAO, (2006). Also, core samples were collected for bulk density determination. The samples were prepared for laboratory analyses.

Laboratory analyses

Particle size distribution was determined by hydrometer method (Gee and Or, 2002). Bulk density was determined by core method (Grossman and Reinsch, 2002). Saturated hydraulic conductivity was determined using a constant head method (Klute, 1986). Soil pH was determined using 1:2.5 soil – liquid ratio using a pH meter (Thomas, 1996). Organic carbon was determined by wet digestion method (Nelson and Sommers, 1982). Total nitrogen was determined by micro-Kjeldah digestion technique (Bremner, 1996). Available phosphorous was determined using Bray II method (Olsen and Sommers, 1982). Exchangeable acidity was determined by the method described by MacLean (1982). Exchangeable bases were determined by neutral ammonium acetate procedure buffered at pH 7.0 (Thomas, 1982). Available micro nutrients (Fe, Pb, Mn and Zn) were extracted by DTPA as described by Sahlemedhin and Taye, (2000) and all these micro nutrients were measured by atomic absorption spectrophotometer.

Statistical analyses

Coefficient of variation as used by Wilding *et al.* (1994) was used to estimate the degree of variability existing among soil properties in the study sites where $CV < 15\%$ = low variation, $CV \geq 15\% \leq 35\%$ = moderate variation, $CV > 35\%$ = high variation. Correlation was also used to compare relationship between selected soil parameters.

Results and Discussion

The result (Table 1) indicated that sand fraction recorded (712 – 792) g kg⁻¹ and (682 – 793) g kg⁻¹ in pedon 1 and pedon 2, respectively. Sand fraction also recorded low variation (4.80 %, 9.20 %) in both pedons. The sand decreased down the profile with no specific trend in pedon 1 while in pedon 2 it decreased in a specific trend. It was observed that the highest sand fraction was indicated in the Ap and AB horizons of pedon 1 and Ap horizon of pedon 2. The predominance of sand over other soil fractions could be attributed to parent material, climate and land-uses. This is in concurrence with the findings of (Obasi *et al.*, 2015) on soils underlain by

coastal plain sand in some agro-ecology in southeastern Nigeria. The low variation could be associated with homogeneity of the soil. Soil with high sand content are associated with nutrient leaching, high infiltration and infertility.

Table 1. Soil physical properties of the studied site

Horizon	Depth cm	Sand	Silt g kg ⁻¹	Clay	TC	Ksat cm/m	BD g cm ⁻³	Po %
Pedon 1								
Ap	0-30	792.0	40.0	168.0	SL	0.0334	1.14	54.81
AB	30-60	792.0	20.0	188.0	SL	0.0198	1.52	59.60
Bt ₁	60-90	772.0	20.0	208.0	SCL	0.0114	1.64	48.25
Bt ₂	90-120	712.0	60.0	228.0	SCL	0.0194	1.58	55.18
Bct	120-180	732.0	40.0	228.0	SCL	0.0430	1.79	58.46
Mean		760.0	36.0	240.0		0.0300	1.53	55.26
CV		4.80	46.48	12.78		49.69	15.78	8.01
Pedon 2								
Ap	0-20	793.0	40.0	167.0	SL	0.0491	1.59	42.59
AB	20-50	782.0	30.0	188.0	SL	0.0480	1.59	42.40
Bt ₁	50-75	752.0	20.0	228.0	SCL	0.0582	1.69	21.86
Bt ₂	75-105	692.0	60.0	248.0	SCL	0.0590	1.70	21.86
Bct	105-180	632.0	10.0	268.0	SCL	0.0690	1.70	21.56
Mean		730.2	32.0	219.8		0.0600	1.65	30.05
CV		9.20	60.11	19.01		15.09	3.54	37.79

TC= textural class, SL= sandy loam, SCL= sandy clay loam, Ksat= saturated hydraulic conductivity, BD= bulk density, Po= porosity

Silt fraction recorded high variation in both pedons (46.48 %, 60.11 %) but also had no specific trend of decrease with soil depth. The high variation could be associated to intense rainfall that facilitated sorting of soil particles. The silt content is in conformity with the findings of Madueke *et al.* (2012) that soils of southeastern Nigeria are low in silt as a result of the high degree and extent of weathering and leaching they have undergone.

Clay fraction (Table 1) recorded (168 – 223) g kg⁻¹ and (167 - 268) g kg⁻¹ in pedon 1 and 2, respectively. However, clay increased down the profile while it recorded low variation in pedon 1 and moderate variation in pedon 2. The clay content of the soils increases with the increasing rainfall and annual temperature. The variation could be attributed to rate of clay migration, drainage pattern and soil structure. However, Obi and Akinbola (2009) reported that increase in clay with soil depth could be attributed to clay translocation and erosion in surface horizon. This is similar to the findings of (Osujieke *et al.*, 2017) in soils of southeastern Nigeria. It was observed that the Bt horizon had high clay content which is an indication of its argillic properties. Higher clay content in the subsurface than the surface horizons in the pedons with subsequent formation of argillic subsurface horizon may be attributed to sorting of soil materials by eluviations and illuviation processes of soil formation.

K_{sat} recorded mean of 0.03 cm m⁻¹ and 0.06 cm m⁻¹ for pedon 1 and 2 but was very slow according to the rating (<0.2 cm m⁻¹) of Landon, (1991). K_{sat} is influenced by soil texture and structure which in turn is influenced by total porosity and pore size distribution. Also, K_{sat} recorded high variation (49.69 %) in pedon 1 and moderate variation (15.09 %) in pedon 2. The rate of variation could be associated with soil texture, bulk density, available pore spaces and intense rainfall. The result showed that soils of Bct horizon conducts more water over other horizons in both pedons. The implication of slow hydraulic conductivity in soils is that the soil will have high runoff and more erosion.

Bulk density (Table 1) recorded (1.14 - 1.79) g cm⁻³ and (1.59 - 1.70) g cm⁻³ in pedon 1 and 2, respectively. Also, bulk density increased down the profile but with an irregular trend in pedon 1. The bulk density values in this soil unit were lower than 1.85 g cm⁻³, a value considered as very high by SSS, (2006) to impede root penetration. However, the value of bulk density is low when compared with findings of (Onweremadu *et al.*, 2011) in soils of southeastern Nigeria. However, the lower values at the surface soil were probably due to presence of organic matter content. The increase in bulk density with profile depth could be associated to decrease in organic matter content, less aggregation and compaction caused by the weight of the overlying soil layers, presence of parent material and low faunal and root activities. Low bulk density influences high porosity which is an indication that soils are not compacted.

Soil pH (Table 2) was slightly-strongly acidic in both pedons according to the ratings of Chude *et al.* (2011). The pH had an irregular pattern of distribution with soil depth. The AB and Bct horizon is the least and most acidic, respectively. Soil pH recorded low variation (12.60 %, 9.52 %) in both pedons which may have resulted from the parent material and intense rainfall which wash off most basic cations. Several researchers (Ndukwu *et al.*, 2012) have reported on low variation of soils of eastern Nigeria and it is the consequence of acidic nature of the parent rocks, coupled with the influence of the leached profile under high annual rainfall condition.

Organic carbon was low according to the ratings of (Akinrinde and Obigbesan, 2000) and recorded range of 0.14 % - 0.64 % and 0.18 % - 0.63 % in pedon 1 and 2. However, the level of organic carbon of the studied pedons was low compared with the findings (Amanze *et al.*, 2016) on soils of southeast Nigeria. Also, Ogeh and Ukodo, (2012) reported low OC in soils of

rainforest zone of Nigeria. Organic carbon (Table 2) recorded high variation (56.42 %, 79.20 %) which could be attributed to higher organic matter deposit on soil surface, rate of decomposition and leaching due to intense rainfall. This is conformity with the findings of (Ukaegbu *et al.*, 2015) on soils of southeast Nigeria. However, OC decreased down the profile but with an irregular pattern in pedon 2. The Ap and B_{tl} horizon recorded the highest level of OC in pedon 1 and 2, respectively. The OC content on Ap horizon could be attributed to the organic material deposited on the surface horizon while that of the B_{tl} could be as a result of other carbon attributors in the soil.

Total nitrogen had range of 0.056 % - 0.07 % and 0.028 % - 0.098 % in pedon 1 and 2, respectively. The total nitrogen level was low according to the ratings of (Enwezor, 1990). The low content of total N in the soils could be attributed to low organic matter of these soils, since inorganic N is accounting for only a small portion of total N in soils (Almu and Audu 2001). The low amount of total N reflects the amount of organic carbon in the soils. Nitrogen can be introduced into the soils by natural processes such as lightening, decay of animal and plant tissues while the main cause of N deficiency in tropical soils is intense leaching and erosion due to the intense tropical rainfall.

Available phosphorus recorded mean of 21.74 mg kg⁻¹ and 18.25 mg kg⁻¹ in the studied pedons and were high according to the ratings (>15 mg kg⁻¹) of (Enwezor, 1990). Available P was high compare with the findings of (Osujieke *et al.*, 2016) in soils of southeast Nigeria. The available phosphorus recorded moderate variation (20.70 %, 23.09 %) in both pedons which could be attributed to organic material deposit, rate of fixation and leaching. The result is contrary to the findings of (Busari *et al.*, 2005; Uzoho and Oti, 2005) that have reported high P deficiency for tropical soils.

Exchangeable bases (Ca, Mg, Na, K) recorded mean of (2.25, 1.29, 0.095, 0.104) cmol kg⁻¹ in pedon 1 and (2.64, 1.40, 0.08, 0.09) cmol kg⁻¹ in pedon 2. Ca was low, Mg was moderate, Na and K were very low according to the rating of Landon (1991). The levels of exchangeable cations are dependent on the nature of parent materials and extent of weathering. The exchangeable bases were within the range reported by Amanze *et al.* (2016) in soils of southeast Nigeria. Exchangeable cations had no specific trend of distribution down the profile pits. The Ca and Mg had low variation in both pedons while Na and K had low variation in pedon 1 and high variation in pedon 2. The variation among the exchangeable cations is associated with leaching and runoff wash of the basic cations, pH level of the soil and fixation rate of the cations.

Cation exchange capacity had range of (2.20 – 4.40) cmol kg⁻¹ in pedon 1 and (3.00 – 4.40) cmol kg⁻¹ in pedon 2. CEC was low according to the ratings of (Esu, 1991) on tropical soil. The CEC result was low compared with the works of (Amanze *et al.*, 2016) on soils of southeast Nigeria. The low CEC could be due to the domination of low activity clay such as kaolinite in these soils which resulted from highly weathered parent rock. This is in concurrence with the finding of Akinrinde and Obigbesan, (2000) on soils of southern Nigeria. Also, Ukpong, (2000) stated that low level of cation exchange capacity in soils could be associated with tidal imports, runoff and seepage. However, CEC decreased down the profile in no specific trend. The Ap horizon

recorded the highest level of CEC which suggested that organic matter could have been its major attribute. The CEC had moderate variation (29.06 %, 16.40 %) in pedon 1 and 2 which could be associated with organic matter level and runoff. Hence, (Enwezor, 1990; Esu, 1991) reported that organic matter is the major attribute of CEC in soils of southeastern Nigeria. Lombin *et al.* (1991) also reported that organic matter content was a major contributor to the CEC of the soil. Therefore, there is need to incorporate organic material into the soil to enhance the exchange site.

Available Fe was below the critical limit recommended by (Kparmwang *et al.*, 2000, Deb and Sakal, 2002). The Fe content was low compared with the findings of (Ahukaemere *et al.*, 2016; Ndukwu *et al.*, 2016) on soils of southeastern Nigeria but was high when compared with the findings of (Mulima *et al.*, 2015) in soils of Northeast Nigeria. The coefficient of variation showed that available Fe recorded high variation (37.82 %) in pedon 1 and moderate variation (32.77 %) in pedon 2. The variation could be associated with rate of mineralization and intense rainfall activities which is associated with study area. Fe content decreased down the profile but had no specific trend in pedon 1.

Lead (Pb) recorded (0.089 – 0.630) mg kg⁻¹ in pedon 1 and (0.216 – 0.658) mg kg⁻¹ in pedon 2. The Pb content was above the critical limit recommended by (Deb and Sakal, 2002; Esu, 1991). Pb recorded high variation (72.67 %, 46.57 %) in both pedons which be attributed to the fixation rate and the amount released by organic matter and mineral matter. The Pb decreased down the profile in an irregular trend. The Pb level was lower than the result reported by (Osakwe and Okolie, 2015; Das *et al.*, 2015) in soils of southern Nigeria. The lead level of the soil is not at toxicity level and thereby will not be harmful to the soil

Mn recorded mean of 2.56 mg kg⁻¹ and 2.27 mg kg⁻¹ for soils under pedon 1 and 2, respectively. Mn was below the critical limit recommended by (Sims and Johnson, 1991). Hence, the available Mn is suitable for crop production and environmentally friendly. It had an irregular pattern of decrease with soil depth and recorded the highest level in B_{t1} horizon in Pedon 1 and Ap horizon in pedon 2. These values are within the range values reported by (Udoh *et al.*, 2008) in soils of southern Nigeria. However, Mn had moderate variation (27.53 %) in pedon 1 and low variation (10.86 %) in pedon 2. The variation could be attributed to soil textural class and rate of porosity. The AB horizon had the least Mn in both pedons while the B_{t1} horizon recorded the highest level of Mn in pedon 1 while the Ap horizon recorded the highest Mn level in pedon 2.

Zinc recorded range of (0.245 – 0.640) mg kg⁻¹ in pedon 1 and (0.247 – 0.520) mg kg⁻¹ in pedon 2 with no specific trend of increase down the profile. Zn level is below the critical limit according to the ratings of (Esu, 1991; Kparmwang *et al.*, 2000; Deb and Sakal, 2002) which is an indication of non toxicity in the soil and as such will pose no threat to the environment. The value of Zn are below the range reported by (Udoh *et al.*, 2008) in soil of southeastern Nigeria but above the range reported by Oyinlola and Chude, (2010) in soils of Northeastern Nigeria. The available Zn was more predominant at the B horizons which could be attributed to illuviation of materials.

Table 2. Soil chemical properties of the studied site

Horizon	Depth cm	pH(H ₂ O)	OC →	TN ←	Av.P ←	Ca	Mg	Na	K →	TEA ←	CEC	BS (%)	Fe ←	Pb →	Mn ←	Zn ←
Pedon 1																
Ap	0-30	5.11	0.64	0.056	24.30	2.80	1.26	0.078	0.102	1.06	4.40	79.81	3.68	0.630	2.691	0.320
AB	30-60	6.26	0.55	0.07	28.10	2.40	0.80	0.082	0.122	0.97	3.20	72.43	3.05	0.284	1.843	0.245
Bt ₁	60-90	5.48	0.27	0.042	16.60	1.60	1.20	0.113	0.112	0.70	2.40	81.12	3.05	0.145	3.702	0.280
Bt ₂	90-120	5.72	0.27	0.028	19.40	2.46	1.60	0.087	0.097	0.53	2.80	88.80	1.28	0.300	2.325	0.640
Bct	120-180	4.44	0.14	0.014	20.30	2.00	1.60	0.113	0.087	0.35	2.20	91.52	1.88	0.089	2.246	0.440
Mean		5.40	0.37	0.03	21.74	2.25	1.29	0.095	0.104	0.72	3.00	82.74	2.59	0.29	2.56	0.39
CV		12.60	56.42	79.58	20.70	20.52	25.71	18.07	12.99	41.06	29.06	9.19	37.82	72.67	27.53	41.66
Pedon 2																
Ap	0-20	5.12	0.63	0.055	24.20	2.80	1.20	0.018	0.102	1.05	4.40	79.81	3.69	0.633	2.593	0.331
AB	20-50	6.20	0.54	0.069	20.96	2.40	0.80	0.080	0.122	0.94	3.20	72.43	3.17	0.285	1.942	0.247
Bt ₁	50-75	5.28	1.60	0.098	16.80	2.80	1.20	0.122	0.123	0.70	3.00	85.78	2.16	0.375	2.255	0.520
Bt ₂	75-105	5.66	0.46	0.056	15.00	2.40	1.80	0.096	0.071	0.80	3.80	84.65	1.87	0.216	2.415	0.490
Bct	105-180	4.88	0.18	0.028	14.30	2.80	2.00	0.104	0.041	0.88	4.20	84.89	1.85	0.658	2.165	0.410
Mean		5.43	0.68	0.060	18.25	2.64	1.40	0.08	0.09	0.87	3.72	81.51	2.55	0.43	2.27	0.40
CV		9.52	79.20	41.52	23.09	8.30	34.99	47.47	38.52	15.26	16.40	6.85	32.77	46.57	10.86	28.19

OC= organic carbon, TN= total nitrogen, Av.P= available phosphorus, TEA= total exchangeable acidity, CEC= cation exchange capacity, BS= base saturation

Table 3. Correlation matrix of selected soil properties of the studied pedons

	Sand	Silt	Clay	Ksat	BD	Po	pH	OC	TN	Av.P	CEC	BS	Fe	Pb	Mn	Zn
Sand	1															
Silt	-0.038	1														
Clay	-0.934**	-	1													
Ksat	-0.517	0.032	0.442	1												
BD	-0.502	0.103	0.665*	0.350	1											
Po	0.564	0.097	-0.582	-0.804**	-	1										
pH	0.333	0.042	-0.269	0.361	0.403	0.103	1									
OC	0.340	-	-0.191	0.267	0.178	-0.385	0.126	1								
TN	0.239	0.200	-0.041	0.211	0.117	-0.439	0.537	-0.713*	1							
Av.P	0.753*	0.286	-0.829**	-0.451	0.570	0.726*	0.286	0.053	-	1						
CEC	-0.072	0.029	-0.210	0.473	-	-0.357	-0.068	0.116	0.016	0.147	1					
BS	-0.600	0.348	0.641*	0.206	0.451	-0.169	-0.708*	-0.132	0.090	-	-0.290	1				
Fe	-0.802	-	-0.883**	-0.220	0.438	0.294	0.179	0.183	0.391	0.567	0.393	-0.747**	1			
Pb	-0.068	0.267	-0.208	0.395	0.606	-0.268	-0.234	0.195	0.084	0.627	0.877**	-0.169	0.351	1		
Mn	0.626	0.207	-0.132	-0.420	0.486	0.079	-0.230	-0.151	0.139	-	-0.133	0.146	0.260	-0.103	1	
Zn	-0.584	0.006	0.519	0.205	0.116	-0.282	-0.267	0.104	0.270	0.265	-0.176	0.822	-0.838**	-0.100	-0.127	1
					0.333				0.082	0.500						

BD= bulk density, OC= organic carbon, TN= total nitrogen, Av.P= available phosphorus, CEC= cation exchange capacity, BS= base saturation, **= Correlation is significant at the 0.01 level, *= Correlation is significant at the 0.05 level.

The sand fraction had positive and significant correlation ($r = 0.753$, $p = 0.05$) with the available phosphorus while it had negative and highly significant relationship ($r = -0.934$, $p = 0.01$) with the clay fraction. The clay fraction had positive and significant relationship with the bulk density ($r = 0.665$, $p = 0.05$) and the base saturation ($r = 0.641$, $p = 0.05$), while it had negative and highly significant relationship with available phosphorus ($r = -0.829$, $p = 0.01$) and Fe ($r = -0.883$, $p = 0.01$). Ksat had negative and highly significant relationship ($r = -0.804$, $p = -0.01$) with total porosity. This relationship may be associated to the textural composition of the soil.

However, Brady and Weil (2002) stated that the rate of hydraulic conductivity is dependent on soil pores. The pH had negative and significant relationship ($r = -0.708$, $p = 0.05$) with base saturation. This relationship could be associated to the leaching of most of the base forming cations thereby leaving the exchange complex dominated by acidic cations. However, the pH had negative relationship ($r = -0.234$, $r = -0.230$, $r = -0.267$) with Pb, Mn and Zn but related positively ($r = 0.179$) with Fe. Organic carbon correlated negatively and significantly ($r = -0.713$, $p = 0.05$) with total nitrogen. This may be due to the factor of age of the soil organic matter, the prevailing climatic condition, N-leaching and volatilization and microbial N-assimilation. The CEC correlated positively and highly significantly ($r = 0.877$, $p = 0.01$) with Pb. Bulk density correlated significantly positive ($r = 0.665$, $p = 0.05$) with clay but had negative correlation ($r = -0.117$) with OC. However, Fe had negative and highly significant relationship ($r = -0.883$, $r = -0.747$, $r = -0.838$, $p = 0.01$) with clay, base saturation and Zn. However, the positive correlation implies that increase in one soil property increases the other while, negative correlation implies that increase in one soil property decreases the other and vice versa

Conclusion

This study has shown soil physicochemical properties and the variation among the horizons of the studied pedons. The organic carbon, total nitrogen, and exchangeable basic cation (Ca, Na, K) were predominantly low while available phosphorus was high. Also, Fe, Mn and Zn were below the critical limit required in the soil. Soil properties must be considered for sustainable agriculture and proper land management practices that will promote the environment. Application of organic matter will be essential for most of the nitrogen and basic cation to be utilized by crops for quality productivity.

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Reference

- Ahukaemere, C.M., B.U. Uzoho, I.F. Irokwe, B.N. Ndukwu, D.N. Osujieke, 2016. Iron, zinc, copper and manganese Availability in four contrasting hydromorphic Soils of Egbema, South-Eastern Nigeria. *Agrochemistry and Soil Science*. No. 85. Kharkiv: NSC ISSAR, Pp. 27 – 34.
- Akamigbo, F.O.R., C.L.A. Asadu, 1983. Influence of parent materials on soil southeastern Nigeria. *East African Forestry Journal*, 48: 8 – 11.

Akinrinde, E.A., G.O. Obigbeson. 2000. Evaluation of fertility status of selected soils for crop production in five ecological areas of Nigeria. Proc. 26th Annual Conf. Soil. Sci. Soc. Nig. Ibadan, Oyo State. Pp. 279 – 288.

Almu, H., M.D. Audu. 2001, Physico-chemical properties of soil of Awa irrigation project are of Kano State. Department of Soil Science, Kano University of Technology Wodi in: Proceedings of the 27th Annual Conference of Soil Science Society of Nigeria. Pp. 13 – 25.

Amanze, C.T., P.C. Oguike, G. Lekwa, 2016. Characterization and classification of soils at Mbari Ubowlla, Emekuku in Owerri North LGA, Imo State. Nig. J. Soil and Env. Res. Vol. 14: 245 – 255.

Arnold, R.W., 1996. Soil Survey Reliability: Minimizing the Consumer's risk in W. G. Nettleton, A. G. Hornsby, R. B. Broen, & T. L. Coleman (eds), Data Reliability and Risk Assessment in Soil Interpretations. SSSA Spec. Publ. 47, SSSA, Madison, WI. Pp 13 – 20.

Bremner, J.M., 1996. Nitrogen total. Sparks, D.L. (ed) methods of soils analysis, parts, chemical method. 2nd ed, SSSA Book Series No. 5, SSSA, Madison, WI 1085–1125.

Busari, M.A., F.K. Salako, R.A. Sobulo, M.A. Adetunji, N.J. Bello. 2005. Variation in Soil pH and Maize Yield as Affected by the application of Poultry Manure and Lime. In Managing Soil Resources for Food and Sustainable Environment. Proc. of 29th Annual Conf. Soil Sci. Soc. Nig. Pp 139 – 142.

Chude, V.O., W.B. Malgwi, I.Y. Amapu, A.O. Ano, 2011. Manual on Soil Fertility Assessment. Federal Fertilizer Department. FAO and National programme on Food security, Abuja, Nigeria. Pp. 62.

Das, U., P. N. Vinayachandran, A. Behara, 2016. Formation of the southern Bay of Bengal cold pool, Springer Berlin Heidelberg Vol. 47(5): 2009 – 2023. <https://doi.org/10.1007/s00382-015-2947-9>.

Deb, D.L., R. Sakal, 2002. Micronutrients. In: Indian Society of Soil Science. Indian Research Institute, New Delhi. Pp. 391 – 403.

Enwezor, W.O., A.C. Ohiri, E.E. Opuwahribo, E.J. Udo. 1990. Literature review on soil fertility investigations in Nigeria. Niger Agric. J. 30: 59 – 75.

Esu, I.E., 1991. Detailed soil survey of NIHORT farm at Bunkure Kano state, Nigeria. Institute of Agricultural Research, Zaria. 72p.

FAO, 2006. Guidelines for soil profile description, 5th edition. AGLS, FAO, Rome.

Gee, G.W., G. Or., 2002. Particle size, In: Dane J.H, & Topp, G.C. (eds). Methods of soil analysis. Part 4 Physical methods. Soil Science Society of America Madison, WI, Book Series No. 5 ASA and SSA 255 – 293.

Grossman, R.B., J.G. Reinsch, 2002. Bulk density and linear extensibility in methods of soil analysis part 4. Physical Methods. Book Series. No. 5. ASA and SSA Madison, WI, Pp. 201-228.

Klute, A., 1986. Water retention: laboratory methods analysis. In: Methods of Soil Analysis (Ed. A. Klute). ASA Press, Madison, WI, USA.

Kparmwang, T., V.O. Chude, B.A. Raji, A.C. Odunze, 2000. Extractable micronutrients in some soils developed on sandstone and shale in the Benue valley Nigeria. *Nigeria Journal of Soil Research*. 1: 42 – 48.

Landon, J.R. (Ed), 1991. *Booker tropical soil manual: A Handbook for soil survey and Agricultural land Evaluation in the tropics and subtropics*, Longman Scientific and Technical, Essex, New York. 474p.

Lekwa, G., 1985. Properties, Classification and site suitability evaluation of two soil mapping units in the guinea savanna, Nigeria. *Soil Science Society of Nigeria*. In: Babalola, O. (ed.), *Nigeria journal of soil science*. 91p.

Lombin, L.O.J., J. Adepetu, K.A. Ayotade, 1991. Complementary use of Organic Manures and in Organic Fertilizer in Arable Crop Production. *Organic Fertilizer in the Nigerian Agriculture: Present and Future. Proceedings of a National organic Fertilizer Seminar, Kaduna Nigeria*.

Madueke, C.O., C.L.A. Asadu, E.T. Eshett, F.O.R. Akamigbo, E.C.C. Maduekeh, C. Onyeokoro, E.I. Maduka, P.C. Obi, C.D. Okene, 2012. Characterization and Classification of soils on a toposequence formed from the coastal plain sands of South-eastern Nigeria. *Proceedings of the 36th Annual Conference of Soil Science Society of Nigeria*.

Mahdi, A., H. Mark, 2006. *Integrated Crop Management; Field Soil Variability and Its Impact on Crop Stand Uniformity*: Iowa State University, Iowa, U.S.A.

McLean, E.O., 1982. Aluminum. In: Pages, A.L., Miller, R.H and keeney, D.R. (Eds), *Methods of soil analysis part 2 American society of Agro economy, Madison W.A*. Pp: 978 – 998.

Mulima, I.M., M. Ismaila, K.M. Benisheikh, I. Saminu, 2015. Assessment of micronutrients status of soils under millet cultivation in Geidam Local Government, Yobe State, Nigeria. *Asian Journal of Basic and Applied Sciences Vol. 2 (2)* 32 – 41.

Ndukwu B.N., M.C. Chukwuma, C.M. Idigbor, S.N. Obasi, 2012. Forms and distribution of potassium in soils underlain by three lithologies in southeastern, Nigeria. *International Journal of Agriculture and Rural Development* 15 (2): 1104 – 1108.

Ndukwu B.N., D.N. Osujieke, C.M. Ahukaemere, M.O. Umeh, 2016. Micronutrients And Physicochemical Properties Of Soils Affected By Municipal Solid Wastes In Ekwulobia Southeastern Nigeria. *Journal of Multidisciplinary Engineering Science Studies (JMESS) ISSN: 2458-925X Vol. 2 Issue 11*, 1032 – 1040.

Nelson, D.W., L.E Sommers, 1982. Total carbon and organic matter. In: *Methods of Soil Analysis Part II*. Page, A.L. (Ed.). *Chemical and Microbiological Properties*. Am. Soc. Agron. Madison, WI., Pp: 359 – 580.

NIMET (Nigerian Meteorological Agency), 2015. *Climate Weather and Water Information, for Sustainable Development and Safety*

Obasi, S.N., D.N. Osujieke, P.E. Imadojemu, I.E. Ezendu, 2015. Characterization and Classification of Soils along Otamiri Watershed in Umuagwo, Southeastern Nigeria *FUTO Journal Series Vol. 1(2)*: 62 – 68.

Obi, J.C., G.E. Akinbola, H.F. Anozie, 2009. Distribution of Dithionite and Oxalate – extractable Iron Oxides of a catena in the basement complex soils of Southwestern Nigeria. *Nigerian Journal of Soil Science*. 19(1):100 – 108.

Ogeh, J.S., E. Ukodo, 2012. Profile Distribution of Physical and Chemical Properties in Soils of a Toposequence in Benin, Rainforest of Nigeria. *Nigerian Journal of Basic and Applied Science*, 20(1): 68 – 72.

Ogunkunle, A.O., 1993. Variation of some soil properties along two top sequences on quartile schist and banded genesis in South Nigeria. *Geoderma* 30 (4), 397 – 402.

Oku, E., A. Essoka, E. Thomas, 2010. Variability of soil properties along an udalf toposequence in the humid forest zone of Nigeria. *Kasetsart J. (Nat. Sci.)* 44: 564 – 573.

Olsen, S.R., L.E. Sommers, 1982. Phosphorus In: methods of analysis part 2 (eds). Page, A.L, Miller, R.H., Keeney, D.R. America Society of Agronomy Madison, Wisconsin Pp. 15 – 72.

Onweremadu, E.U., C.M. Ahukaemere, O.A. Orji, 2015. Horizon Differences in Selected Physical Properties of Soils formed Over Dissimilar Lithologies in South-Eastern Nigeria. *FUTO Journal Series (FUTOJNLS) VOL. 1(2)* 55 – 61.

Onweremadu, E.U., J.A. Okuwa, J.D. Njoku, and U.O. Ufot, 2011. Soil nitrogen forms distribution in isohyperthermic Kandiudults of Central southeastern Nigeria. *Nigeria J. Agric. Food and Environ.* 7(2): 52 – 56.

Osakwe, S.A., L.P. Okolie, 2015. Physicochemical Characteristics and Heavy Metals Contents in Soils and Cassava Plants from Farmlands along A Major Highway in Delta State, Nigeria. *Nigeria J. Appl. Sci. Environ. Manage.* Vol. 19 (4) 695 – 704.

Osujieke, D.N., P.E. Imadojemu, J.N. Igbojionu, 2017. Characterization and variability of soils formed on a toposequential floodplain in Uratta, Southeastern Nigeria. *FUW Trends in Science and Technology Journal*. Vol. 2(1B): 628 – 632.

Osujieke, D.N., E.U. Onweremadu, C.M. Ahukaemere, B.N. Ndukwu, 2016. Classification of soils of a toposequence underlain by coastal plain sand in South-east Nigeria. *Nig. J. Soil and Env. Res.* Vol. 14: 256 – 263.

Oyinlola, E.Y., V.O. Chude, 2010. Status of available micronutrients of the basement complex rock – derived alfisols in northern Nigeria savanna. *Tropical and Subtropical Agro ecosystems*, 12: 229 – 237.

Sahlemedhin, S., B. Taye, 2000. Procedures for soil and plant analysis. National Soil Research Centre, Ethiopian Agricultural Research Organization, Addis Ababa, Ethiopia. 110p.

Sims, J.T., G.V. Johnson, 1991. Micronutrient soil tests. In: J.J. Mortved. F.R. Cox, R.M. Welch. (Editors). *Soil Sci. Soc. Am. Inc. Madison, Wisconsin, USA*. Science 6(2): 93 – 100.

Soil Survey Staff, 2006. Soil quality information sheet; soil quality indicators aggregate stability. National Soil Survey Centre in collaboration with NRCS, USDA and the National Soil Tilth Laboratory. ARS, USDA.

Thomas, G.W., 1982. Exchangeable cations. In: A. L. Page; R. H. Miller and D. R. Keeney (eds.). *Methods of Soil Analysis, Part 2, Chemical and Microbiological properties*. Madison, Wisconsin. Pp. 159 – 164.

Thomas, G.W., 1996. Soil pH and Soil Acidity. In: *Methods of soil analysis, part 3- Chemical methods*. L.D. Sparks (eds) SSSA book series 159 – 165.

Udoh, B.T., T.O. Ibia, B.U. Udo, S.O. Edem, 2008. Assessment of micronutrient status of inland depression and floodplain (wetland) soils in Akwa Ibom State Southeastern Nigeria. *Journal of Tropical Agriculture, Food, Environment and Extension*. Vol 7 (2): 156 – 161.

Ukaegbu, E.P., S.K., Osuaku, and C.C. Okolo, 2015. Suitability assessment of soils supporting oilpalm plantations in the coastal plains sand, Imo state, Nigeria. *NJSS* Vol. 25: 125 – 134.

Ukpong, I.E., 2000. Ecological classification of Nigeria mangroves using soil nutrient gradient analysis. *Wetlands Ecol. Manage.*, 8: 263 – 272.

Uzoho, B.U., N.N. Oti, 2005. Phosphorus adsorption characteristics of selected Southeastern Nigerian soils. *Agro-Sci. J. Agric. Food, Environ. Ext.* 4(1):50 – 55.

Wilding, L.P., J. Bouma, D.W. Boss, 1994. Impact of spatial variability on interpretative modeling. In: *Quantitative modeling of soil forming processes*. Bryant, R.B. and Arnold, R.W. SSSA. Special publication. No.39: 61.



Sulphur Balance in Agroecosystem

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Abstract

This field study shows how different crops and soil treatments with different nitrogen fertilization levels affect sulphur balance. Sulphur deposition, leaching through soil and water seepage, availability and uptake by crops, effects on crop yield and losses were investigated. The research was conducted on a field trial from 1996 to 2014 in temperate continental climate on Stagnosols. The soil was treated 10 times with mineral nitrogen fertilizers in an ascending doses from 0 to 300 kg N ha⁻¹ and additional two 250 kg N ha⁻¹ treatments, one with phosphogypsum and one with zeolite tuff and CaCO₃. Drainpipes and lysimeters were installed to collect water samples and measure the effects of N doses, amendments and precipitation on sulphur losses. Average annual sulphur losses were from 4.9 to 68.7 kg ha⁻¹ through drainage water, and from 1.5 to 24.9 kg ha⁻¹ through lysimeter water. Depending on a crop, year and yield, average crop losses ranged from minimal 2.8 kg ha⁻¹ in winter wheat up to 17.6 kg ha⁻¹ in oilseed rape. Average total S content in soil varied from 882 to 1764 kg ha⁻¹. Overall agroecosystem S balance between input and output, calculated for all crops and all treatments was positive only in the treatment with phosphogypsum for winter wheat, corn and oilseed rape. Water shortage in 2011 caused positive S balance for soybean in other treatments too, not only in the treatment where phosphogypsum was applied.

Key words: phosphogypsum application, mineral nitrogen fertilization, crops, drainage and lysimeter water, soil, atmospheric deposition

Introduction

The presence of sulphur in the soil is in the form of organic compounds, sulphides (S⁻), elemental sulphur (S⁰) and sulphate (SO₄²⁻). According to Isaac, Kerber (1971), a normal concentration range of total sulphur in soils is from 500 mg kg⁻¹ to 4000 mg kg⁻¹. Total sulphur in mineral soils may range from < 20 mg kg⁻¹ in sandy soils up to > 600 mg kg⁻¹ in heavy texture soils. Organic soils may contain as much as 5000 mg kg⁻¹ (Zgorelec et al., 2012). Most soils, however, contain between 100 and 500 mg kg⁻¹ of sulphur. Elemental sulphur must be oxidized by soil bacteria to SO₄²⁻ before becoming plant available. Warm temperatures and good moisture and aeration are required for S-oxidizing bacteria to work. Sulphur oxidation is minimal at soil temperatures that are less than 10 °C. Even at 23 °C, sulphur oxidation rate is about 15 % of the oxidation taking place at 29 °C, therefore the peak rates of sulphur oxidation do not occur until late spring (Camberato et al., 2012). After

sulphur is oxidized into sulphate, plants absorb it and it is converted into amino acids cysteine and methionine. These amino acids are the building blocks of sulphur based proteins and other key role compounds in multiple plant functions like photosynthesis, disease resistance and plant growth. Because of its important roles, optimizing the sulphur nutrition of crops is key to achieve top crop yields and quality. Since the early 1960s, the research on the response of crops to sulphur expanded over years and covered a large number of crops, soils and fertilizers. By 1990, it was clear that sulphur deficiencies were becoming increasingly important as evidenced not only by soil analyses but, more importantly, by the results of field research which documented effects of sulphur application to about 30 crops under various weather conditions and on various types of soil (Tandon, 2011). Sulphate leaching may be subject to considerable variations caused by differences of pH in the soil. Soils with lower pH value have better adsorption of sulphur. Eriksen et al. (2002) investigated sulphate leaching and S balance in organic cereal crop rotation. It was found that sulphate leaching was quantitatively the most important item of the S balance. On some treatments of nitrogen fertilization, FG was used. In the process of decomposition of raw phosphate with sulfuric acid which was used for phosphoric acid production, FG occurs as by-product. Vyshpolsky et al. (2010) conducted a two-year experiment on the plots of cotton on heavy clay with a 1% content of organic matter, and by applying FG the efficiency of irrigation was increased and water retention around the root system improved.

Given the fact that sulphur has been widely recognized as the fourth major plant nutrient after nitrogen, phosphorus and potassium and cannot do the job alone than it must work as a member of the plant nutrition team, assessment of the sulphur balance in this experiment is significant and gives an idea of the sulphur cycle in the soil-fertilizer-plant system. Sulphur addition with phosphogypsum, amelioration with zeolite tuff and CaCO_3 and fertilization with different nitrogen levels allows the role of sulphur and nitrogen to be monitored for growth, yield and crop quality, to be assessed the impact of pH on sulphur mobility and extraction, and of the plants, as well as sulphur adsorption from the soil. On the other hand, an anthropogenic impact through human influence on agriculture affects the ecosystem in general. Excessive accumulation of sulphur in the soil represents an environmental problem through its deposition on the soil and its leaching in the lower layers of the soil which can lead to soil contamination. Therefore, it is important for us to explore the ecosystem, to have the agroecosystem and to implement management of plant nutrition, but in the same time to protect the ecosystem. Accordingly, the main goal was to determine sulphate losses and gains in a field experiment with a certain soil type and climate including different nitrogen fertilization doses and to valorise and determine an overall sulphur balance in agroecosystem (soil, planted crops, water and air deposition).

Materials and Methods

This research was conducted from 1996 to 2014 in central part of Croatia in Popovaca (Figure 1) where intensive agriculture occurred. Selected location is on the border with Park of nature Lonjsko polje which has natural water retention and needs to be protected. According to Skoric (1986), the type of soil was plain, deep, district drained pseudogley (Stagnosols); deep, district pseudogley according to Husnjak (2014), and district Stagnosols according to FAO, WRB (2006). Excessive humidity was present in the upper part of profile,

because of rainfall, and ground water occurred below 175 cm of depth. The soil was slightly porous throughout its depth, with mediocre capacity for water. Air capacity was very small. The soil was classified as acid (~ 4.5) (Zgorelec et al., 2013). The compaction of soil in the field trial was medium in arable and eluvial, and higher in deeper horizons. Because of these characteristics, drainage pipes were conducted on the surface. The characteristic of the area is continental climate with mean annual temperature of 10.7°C and average rainfall of 865 mm (Zgorelec et al., 2013).

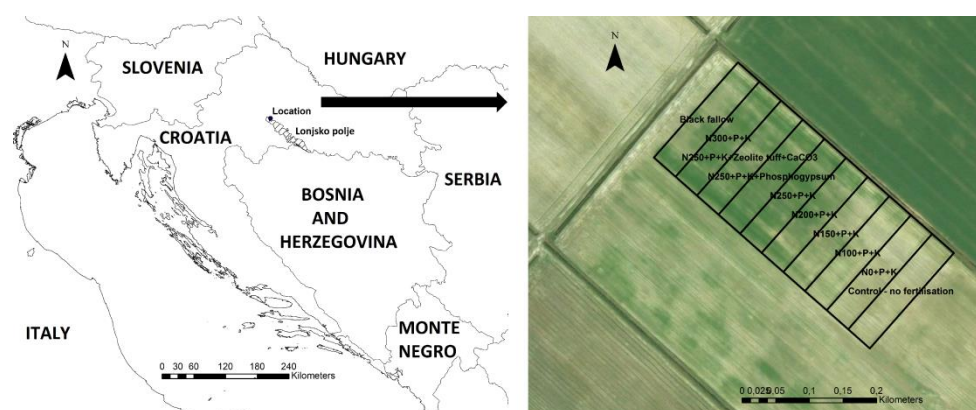


Figure 1. Study location

The trial consisted of 10 treatments with different mineral nitrogen doses. Table 1 presents treatments with different fertilization doses and application time during the experiment.

Table 1. Fertilization (kg ha^{-1}) treatments and application time (per year)

Treatment	Fertilization (kg ha^{-1})	Application period/year
I.	Control - no fertilization	-
II.	0 N + 120 P + 180 K	every year
III.	100 N + 120 P + 180 K	every year
IV.	150 N + 120 P + 180 K	every year
V.	200 N + 120 P + 180 K	every year
VI.	250 N + 120 P + 180 K	every year
VII.	250 N + 120 P + 180 K + 12 t ha⁻¹ Phosphogypsum (FG)	1996, 2002 and 2009
VIII.	250 N + 120 P + 180 K + 3 t ha⁻¹ Zeolite tuff + CaCO₃ (+Dolomite)	1996, 1999, 2002, 2009, (+2013)
IX.	300 N + 120 P + 180 K	every year
X.	Black fallow	-

All agro technical measures including tillage, herbicide applications etc. were identical in all trial treatments.

Soil samples were taken three times per year (2010), at the beginning of the growing season, during the growing season and immediately after the harvest of certain crops (winter wheat). Samples were taken from each treatment at surface horizon (0 – 30 cm). Total S in soil (kg ha^{-1}) was calculated from the measured concentration (mg kg^{-1}) of S in soil and soil bulk density (1.4 g cm^{-3}) determined in arable horizon (0-30 cm). The measurement for total S content in plant material started in 2006. The losses of total sulphur in kg ha^{-1} were calculated

from measured concentration of total sulphur (mg kg^{-1}) in plants and from measured crop yield in kg ha^{-1} . Lysimeters and drainpipes were installed as described in Zgorelec et al. (2013); Vukovic et al. (2008) and Sestak et al. (2014). In drainage and lysimeter water, S-SO_4 concentration in water (mg L^{-1}) and drainage discharge (L day^{-1}) are taken to calculate sulphur losses in kg ha^{-1} (Figure 2 and Figure 3). Table 2 presents parameters determined in soil, plant material and water including determination methods.

Table 2. Parameters determined in soil, plant material and water including determination methods

SOIL	Sampling, transport and storage	Soil quality - Sampling - Guidance on sampling techniques	HRN ISO 10381-1 to 8 (2002-2006)
	drying/grinding/sieving/homogenizing	Soil samples preparation for physical and chemical analysis	HRN ISO 11464:2006
	pH	Soil quality - Determination of pH in 0.01 M CaCl_2 , 1 M KCl and H_2O at 1:2.5 (w/v) ratio	HRN ISO 10390:2004
	TS ($\% \text{ DM}$; g kg^{-1})	Soil quality - Determination of total sulphur with dry combustion method	HRN ISO 15178:2005
PLANT	sampling	Cereals and cereal products - sampling	ISO 24333:2009
	drying/grinding/sieving/homogenizing	Sample preparation for analysis of inorganic chemical composition	modified HRN ISO 11464:2006
	TS ($\% \text{ DM}$; g kg^{-1})	Determination of total sulphur with dry combustion method	modified HRN ISO 15178:2005
WATER	F^- , Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^{2-} and PO_4^{3-} (mg kg^{-1})	Water quality - Determination of fluorides, chlorides, nitrites, orthophosphates, bromides, nitrates and sulphates with ion liquid chromatography - part 1. Method for water with low contamination	HRN ISO 10304-1:1998

The crops grown in crop rotation are presented in Table 3. Considering that measurement of total S content in plant material started in 2006, the collected, analysed and taken into balance account data are marked with the bold text in Table 3.

Table 3. Cultivated crops during the experiment

Crop	Vegetation year
Corn (<i>Zea Mays</i> L.)	1996, 1999, 2004, 2007, 2013
Oilseed rape (<i>Brassica napus</i> L.)	1998, 2001, 2009
Soybean (<i>Glycine</i> L. max)	2002, 2005, 2011
Winter wheat (<i>Triticum aestivum</i> L.)	1997, 2000, 2003, 2006, 2008, 2010, 2012

In this research, quality assessment and control were included. Analytical laboratory of Department of General Agronomy integrates Internal and External quality control. Internal quality control is carried out on a daily basis and involves checking the accuracy and repeatability of measurements by analysing the reference material (RM) and doing a minimum of three consecutive measurements. RM samples from different inter laboratory trials were used in the laboratory: ISE (International Soil analytical Exchange Programme organized by WEPAL [Wageningen Evaluating Programs for Analytical Laboratories, organized by Soil Chemistry and Chemical Soil Quality group, Department of Soil Quality of Wageningen University (WU), Netherlands]) for soil, IPE (International Plant analytical Exchange Programme organized by WEPAL) for plant and IFA (Water Proficiency Testing scheme organized by BOKU, Department for Agrobiotechnology, IFA-Tulln, Center for Analytical Chemistry) for water. External quality control is performed once a year where it participates in various plant, soil and water field testing programs.

Results and Discussion

Drainage water

Figure 2 shows minimum, maximum and average annual $\text{SO}_4\text{-S}$ losses through drainage water which are calculated for each treatment for the period between 1996 and 2014. If treatments VI, VII and VIII, to which the same doses of N, P and K were applied, are compared and if the fact that 335 kg ha^{-1} of S was annually applied through FG in treatment VII, is taken into consideration, the average loss was the highest in treatment with FG (VII), which is 9.4 times higher than the average loss in treatment VI leads to the conclusion that losses of S due to FG application were 61.4 kg ha^{-1} . Furthermore, we revealed that 18.3 % of applied S (in treatment VII) was drained, while the rest was adsorbed by the plant or the soil. Accordingly, Monaghan et al. (2000) investigated nutrient losses in drainage water where leaching losses of sulphate in the 0 N fertilizer treatment was 1.9 times higher (17 kg ha^{-1}) than in this research. In Riley et al. (2002) research, three years experiment recorded total S loss of 34.9 kg ha^{-1} .

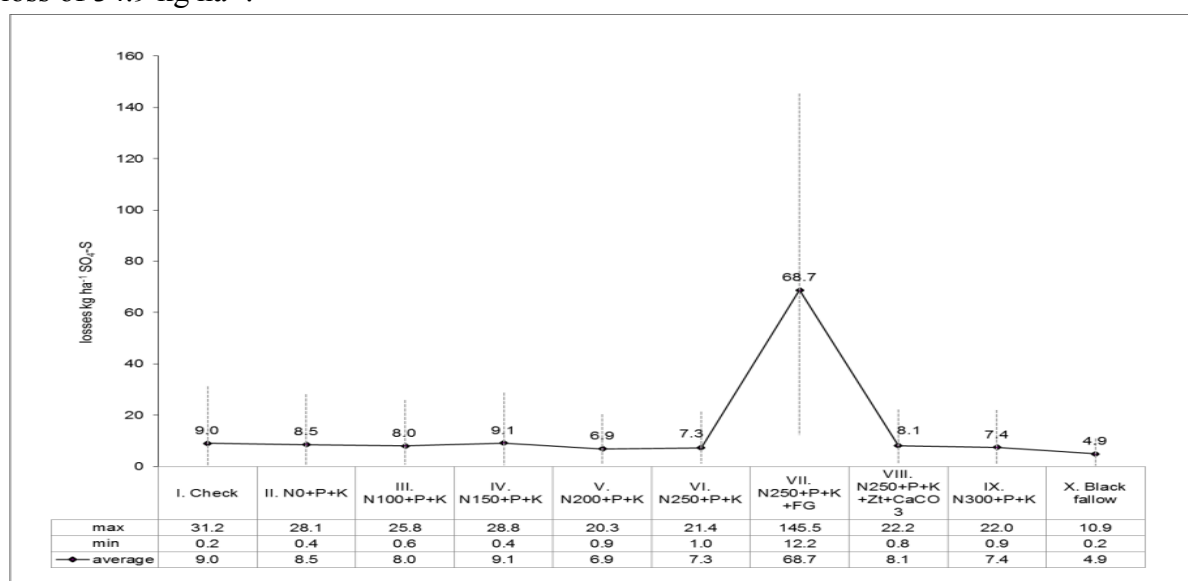


Figure 2. Average annual $\text{SO}_4\text{-S}$ losses through drainage water (from 1996 to 2014); $n=151$

Lysimeter water

Figure 3 shows minimum, maximum and average annual $\text{SO}_4\text{-S}$ losses through lysimeters water which were calculated for each treatment for the period from 1996 to 2014. If treatments VI, VII and VIII, to which the same doses of N, P and K were applied, are compared and if the fact that 335 kg ha^{-1} of S was applied annually through FG in treatment VII, is taken into consideration, the average loss was the highest in treatment with FG (VII), which is 9.7 times higher than the average loss in treatment VI meaning that the input of S to water due to FG was 22.4 kg ha^{-1} . The conclusion is that 6.7 % of applied S gets lost through lysimeter water, while the rest is adsorbed in the soil and/or the plant. Eriksen, Askegaard (2000) found that sulphate leaching from an organic dairy crop rotation, on sandy soil was 20 kg ha^{-1} – average of 4 years, equivalent to 60 % of total sulphur input. In this research, average S loss by lysimeter water calculated for all treatments except treatment VII was 2.0 kg ha^{-1} .

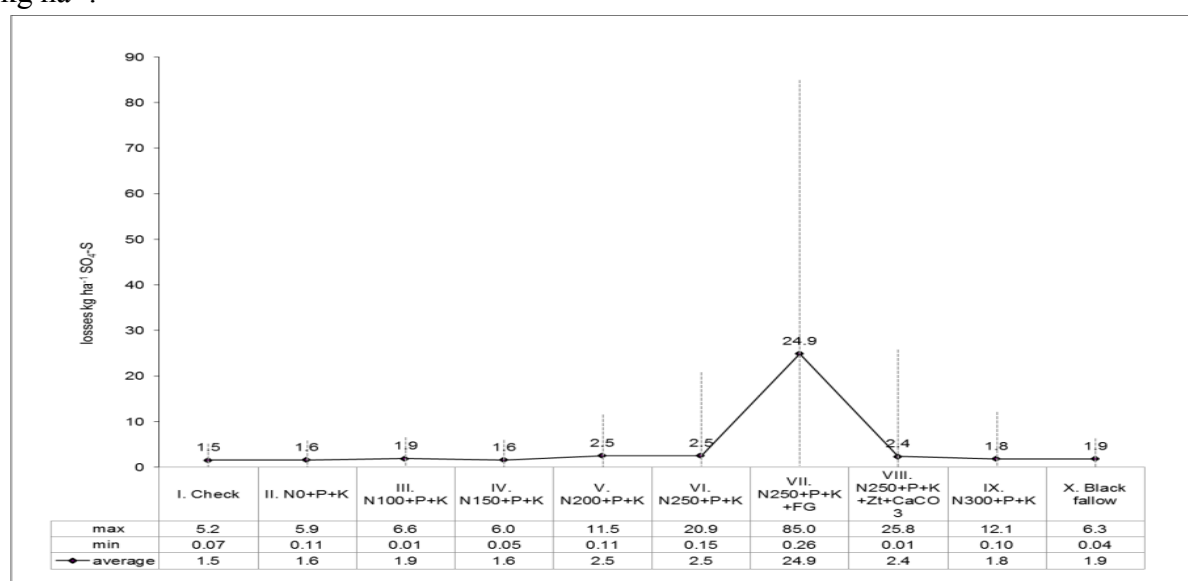


Figure 3. Average annual $\text{SO}_4\text{-S}$ losses through lysimeter water (from 1996 to 2014); $n=124$

Losses of sulphur through crop yields

It is well established that sulphur application not only increases crop yield but also improves crop quality. It improves crop quality in many ways, some of which are: increasing the oil content of seeds, improving nutritional quality of forages by providing a balanced NS ratio, increasing crude protein content, and improving baking quality of wheat (Tandon, 2011). A balanced NS ratio is important because of nitrogen use efficiency, plant vigour, water use efficiency, phosphate use, carbohydrate production and utilization, the rate of grain fill, maturity and many other plant factors. It primarily reflects the complementary relationship that nitrogen and sulphur have in producing plant proteins. On a higher nitrogen fertilization level, the plant uptake of sulphur was higher, because on a high nitrogen level in the soil, sulphur in the soil becomes more mobile, and the plant can easily take it (synergism). The importance of concurrent NS management in wheat was described in Salvagiotti et al. (2009) research. In this research, the highest level of nitrogen fertilizers was applied in treatment IX with $300\text{N} + 120\text{P} + 180\text{K kg ha}^{-1}$. Losses through yield were calculated by sulphur content in crop yield. The lowest S losses were observed in winter wheat at treatment

with $0\text{N} + 120\text{P} + 180\text{K kg ha}^{-1}$ (II), and the highest in oilseed rape at treatment with $250\text{N} + 120\text{P} + 180\text{K kg ha}^{-1} + \text{zeolite tuff} + \text{CaCO}_3$ (VIII) (Figure 4). The sulphur requirements of different crops vary widely. It is reported by Beeson (1941) that legumes utilize large amounts of sulphur for growth, while cereals and similar crops generally have less requirements of sulphur. The author also revealed that sulphur content in wheat (grain/straw) ranged from 1.7 g kg^{-1} to as high as 4.5 g kg^{-1} in sweet clover. In this research, sulphur was also associated with a higher biological N fixation by legumes. The trend of increase in S content in grain due to rising mineral N content in the soil was noticed in Figure 4. For example, in soybean, the application of sulphur increased the number of nodules/plant and nodule weight (Gupta, Dubey 1998; Tiwari, Gupta 2006). Whenever the sulphur status of growing plants drops below the critical level which is different for different cultures, the visual symptoms of sulphur deficiency start appearing on the plant, generally in leaves. In many ways, sulphur deficiency symptoms resemble those of N in the early stages in that the leaves become pale-yellow or light green. The appearance of such symptoms itself indicates a serious condition because crop yields can decrease even without the appearance of such symptoms as a result of hidden hunger (Tandon, 2011). In Figure 4 losses of total sulphur through different crop yield are shown respectively (winter wheat, corn, soybean and oilseed rape).

Table 4. Average sulphur content (g kg^{-1}), annual average yield (t ha^{-1}) and losses of S through yield for all treatments (kg ha^{-1})

	Winter wheat n=144	Corn n=72	Soybean n=36	Oilseed rape n=36
Average sulphur content in yield, g kg^{-1}	2.0	1.8	1.7	4.9
Annual average yield, t ha^{-1}	3.2	6.7	2.7	2.6
Average losses of S through yield, kg ha^{-1}	6.4	12.1	4.6	12.7

In Table 4, average sulphur content in yield, annual average yield and losses of S through yield were calculated for all treatments and all years. Table 4 clearly shows higher S content in oilseed rape than in other crops, while losses of S in oilseed rape were similar to corn, because of higher yield of corn. Sulphur removal by corn, winter wheat, oilseed rape and soybean are presented on Figure 4. Average losses of S through winter wheat yield (Table 4) is in consistence with Beeson's (1941) meaning that harvesting crops with lower percentage of sulphur content may result in annually removal of 6 kg ha^{-1} of sulphur. Sulphur deficiency significantly effects the production and quality of winter wheat (McGrath, 2003; Györi, 2005). Without adequate sulphur, crops cannot reach their full potential in terms of yield, quality or protein content; nor can they make efficient use of applied nitrogen (Sahota, 2006). Eriksen et al. (2002) reported that sulphur output by winter wheat uptake could be up to 4 kg ha^{-1} depending on year and soil type.

According to this research, in Camberato, Casteel (2017) research about 11 kg S ha⁻¹ is removed by corn. The research of sulphur application to corn and soybean crops in Iowa revealed that the combined S supply from soil profile, sulphate, atmospheric deposition, crop residue and organic matter mineralization fulfil corn requirements for sulphur (Sawyer et al., 2002).

For soybean, sulphur requirement is higher especially than in many other crops (Aker et al., 2013). Considering that fact, losses in this research are low compared with other investigated crops (corn, winter wheat and oilseed rape). Received losses can be attributed to yield, which was considerably lower in 2011 due to the intense drought. In Lamond (1997) research, sulphur removal by soybean grain was 13 kg ha⁻¹.

In Eriksen, Mortensen (1999) research, removal of S by oilseed rape was 3.6 and 3.0 kg ha⁻¹, respectively. Oilseed rape has a high demand for sulphur compared with cereals, with approximately 16 kg of sulphur required to produce each tone of seed (HGCA, 1998). Consequently, oilseed rape is particularly sensitive to any shortfall in sulphur supply.

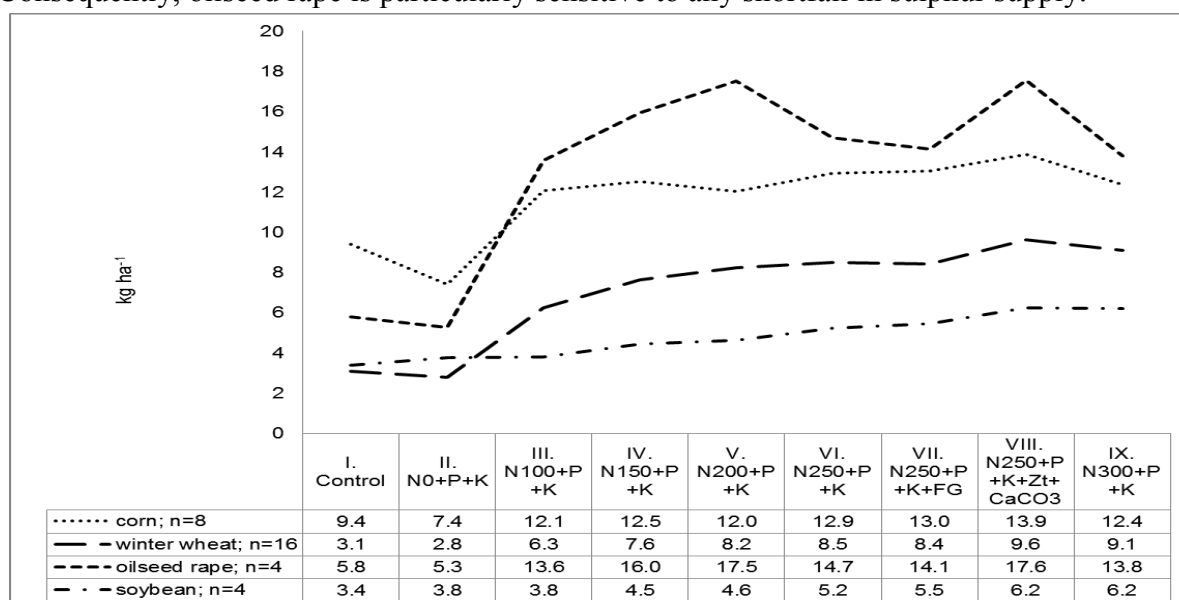


Figure 4. Losses of sulphur through crops yield/grain (corn, n=8; winter wheat, n=16; oilseed rape, n=4; soybean, n=4)

Sulphur content in soil

The main source of S for plants originates from soil. According to Yang et al. (2007), Kotkova et al. (2008), and Förster et al. (2009), the total soil S content depends on fertilizer types applied (mineral or organic manure), and changes in soils have been found to be proportional to the amount of organic residues added. As it is written in the introduction, a normal concentration range of total S content in soils could range from 2 100 kg ha⁻¹ to 16 800 kg ha⁻¹, while in this study the range was from 882 kg ha⁻¹ in control treatment (I), to 1764 kg ha⁻¹ in 250 kg N ha⁻¹ on FG variant (VII) (Figure 5), in soil layer 0 – 30 cm. In total, 36 000 kg FG ha⁻¹ was applied three times every six years, i.e. 12 000 kg FG ha⁻¹ per dose, on treatment VII. Accordingly, the S content that was applied in this study for a total period was 6 698 kg S ha⁻¹, or 335 kg S ha⁻¹ per year. If we compare treatments VI and VII, on which were applied the same doses of NPK but they differ in FG, we observed 462 kg ha⁻¹ more S in the soil on treatment VII with FG than on treatment VI without FG. Considering that FG

contains S, it can be added through the FG application where the exact concentration of S must be determined according to its leaching tendency. In a long-term field experiment conducted by Yang et al. (2007), total S ranged from 1392 kg ha⁻¹ in the control without fertilizer application to 1808 kg ha⁻¹ in the treatment with farmyard manure. In the plots receiving either NK or NPKS fertilizers for more than 80 years, no significant accumulation of total S, as compared with the control, could be detected.

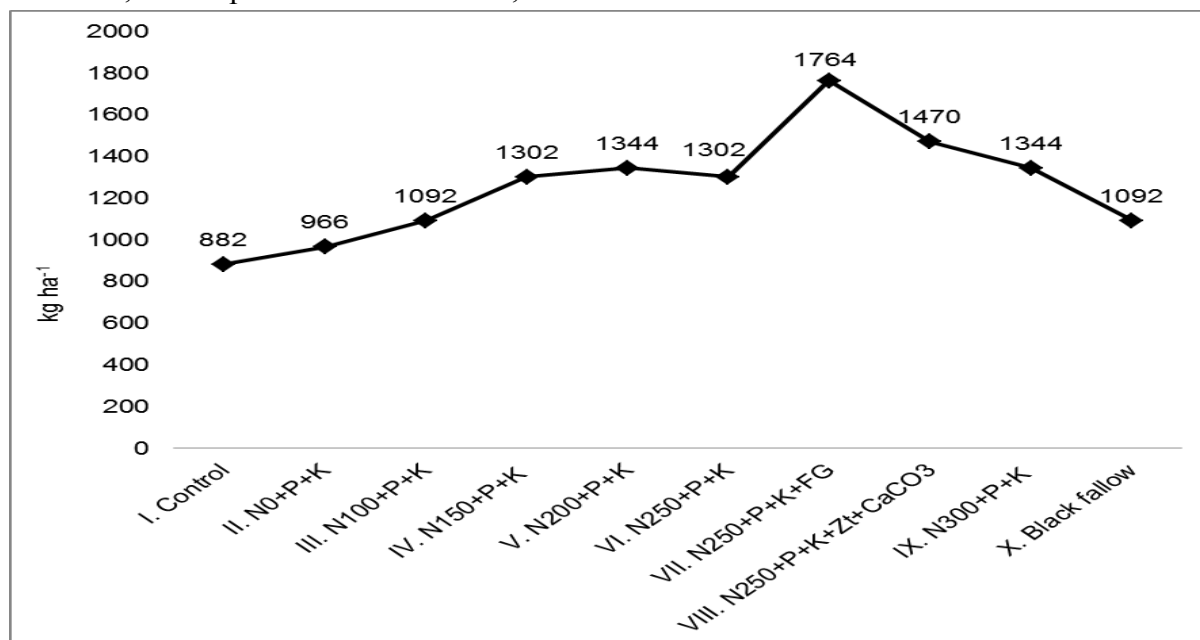


Figure 5. Average sulphur content in soil

Sulphur wet deposition through trial period

Deposition of sulphur compounds is considered a major environmental issue (pollutant) – especially in Europe, where its effects were first observed (Walaszek, 2013). Due to technological development in industry and switching fuels from coal to oil and gas, emissions of oxidized sulphur dropped by 45 % over the last few decades. The removal of pollutants from the atmosphere can occur in one of two ways: by wet deposition or dry deposition (Fagerli, 2008; Giannitrapani, 2006). Erisman et al. (2005) estimated that about 80 % of pollutants deposited in Europe are subject to wet deposition. Wet deposition is a process of washing out pollutants from the air by precipitation or cloud droplets (Walaszek, 2013) and may cause natural vegetation damage (Bytnerowicz et al., 2007), soil and water acidification (Sullivan et al., 2005; Zhao et al., 2009) and water eutrophication (Camargo, Alonso 2006). As it stands in Hu et al. (2005) current inputs of S from atmospheric deposition are less than 10 kg ha⁻¹ in most Western European countries. Annual wet deposition of S – SO₄²⁻ at measuring station Bilogora, which is the nearest to the field trial ranged from 2.6 kg S – SO₄²⁻ ha⁻¹ in 2011 to 10.6 kg S – SO₄²⁻ ha⁻¹ in 2001 (Statistical Yearbook of Republic of Croatia, 2001 - 2015) and shown on Figure 6. An average deposition through this study was 6.0 S – SO₄²⁻ ha⁻¹. Jian et al. (2014) studied atmospheric wet deposition of sulphur in developing and developed areas of South-eastern China and found S deposition in range of 56.02 – 59.06 kg ha⁻¹ per year, respectively, surpassing their corresponding critical loads in China which is incomparably higher than in this research. Knights et al. (2000) reported that

large S inputs from atmospheric deposition and from sulfate fertilizer did not accumulate as organic and inorganic S in arable soils, but organic S obviously increased after FYM supply.

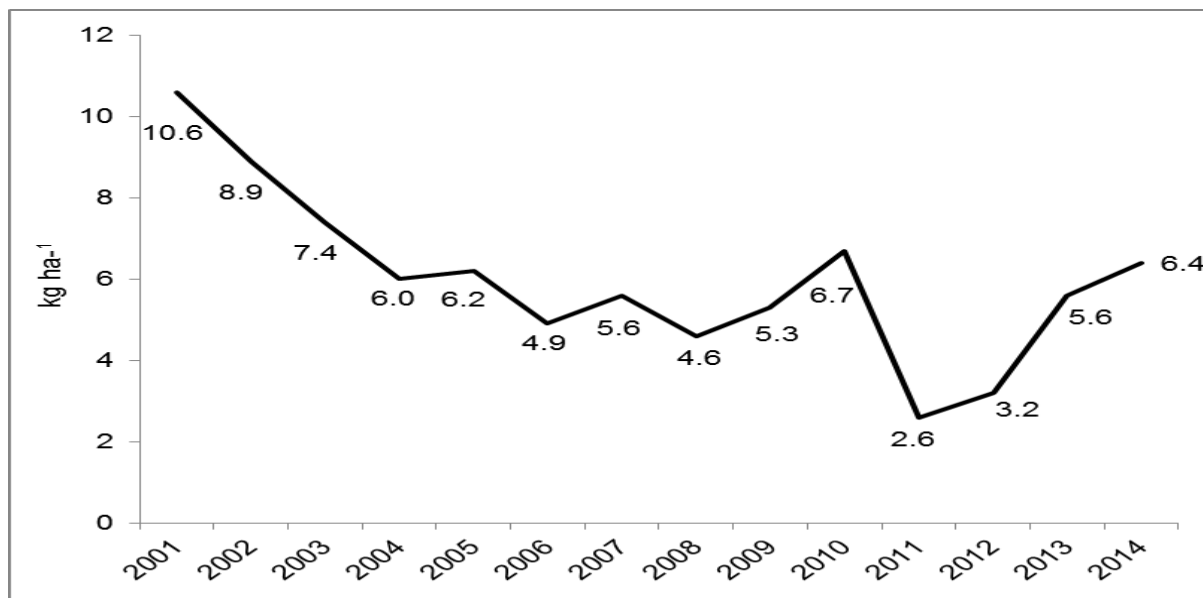


Figure 6. Annual wet deposition of S-SO₄ from 2001 to 2014 (Source: Statistical Yearbook of Republic of Croatia; 2001 - 2015)

Sulphur balance through trial period

Sulphur balance for all investigated crops is shown in Table 5. Volatilization from crops or soil was ignored as the amount of sulphur emitted from these sources was considered insignificant (Janzen, Ellert 1998). The input from atmospheric wet deposition was in average 6.0 kg ha⁻¹ of S-SO₄. The following year, an average sulphur balance was calculated for specific crops: winter wheat – 2006, 2008, 2010, 2012; corn – 2007, 2013; soybean – 2011; oilseed rape – 2009. The results of average losses of drainage water, lysimeter water and removal through yield as output were shown for every year that was taken in calculation. The average wet deposition and FG application were taken as input value of sulphur. The overall sulphur balance was negative, except in treatment where FG was applied.

Table 5 Average sulphur S-SO₄ (kg ha⁻¹) balance per crop

Variants	Winter wheat, n=4										Corn, n=2									
	Input					Output					Input					Output				
	Sulphur content in soil (2010) 0-30 cm	Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	Balance	Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	Balance	Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	Balance	
I	882	6.0	-	2.1	2.9	3.1	-2.1	6.0	-	8.0	5.4	9.4	-16.9	6.0	-	8.0	5.4	9.4	-16.9	
II	996	6.0	-	4.3	2.5	2.8	-3.6	6.0	-	12.6	4.5	7.4	-18.4	6.0	-	12.6	4.5	7.4	-18.4	
III	1092	6.0	-	4.1	2.8	6.3	-7.1	6.0	-	17.1	6.5	12.1	-29.7	6.0	-	17.1	6.5	12.1	-29.7	
IV	1302	6.0	-	4.2	2.8	7.6	-8.7	6.0	-	13.2	5.8	12.5	-25.5	6.0	-	20.9	5.9	12.0	-32.8	
V	1344	6.0	-	5.0	2.3	8.2	-9.6	6.0	-	22.3	6.3	12.9	-35.5	6.0	-	251.3	68.1	13.0	8.6	
VI	1302	6.0	-	7.3	2.6	8.5	-12.4	6.0	-	14.7	7.0	13.9	-29.5	6.0	-	10.9	5.2	12.4	-22.5	
VII	1764	6.0	335.0	54.4	29.4	8.4	248.8	6.0	335.0	7.8	5.8	-	-7.6	6.0	-	7.8	5.8	-	-7.6	
VIII	1470	6.0	-	4.6	4.2	9.6	-12.5	6.0	-					6.0	-					
IX	1344	6.0	-	3.5	1.7	9.1	-8.3	6.0	-					6.0	-					
X	1092	6.0	-	4.4	2.1	-	-0.5	6.0	-					6.0	-					

Variants	Soybean, n=1 (2011)										Oilseed rape, n=1									
	Input					Output					Input					Output				
	Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	Balance	Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	Balance	Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	Balance		
I	6.0	-	-	-	3.4	2.6	6.0	-	-	3.5	4.8	5.8	-8.1	6.0	-	3.5	4.8	5.8	-8.1	
II	6.0	-	-	-	3.8	2.2	6.0	-	-	4.2	4.4	5.3	-7.9	6.0	-	4.2	4.4	5.3	-7.9	
III	6.0	-	-	-	3.8	2.2	6.0	-	-	8.0	3.9	13.6	-19.5	6.0	-	8.0	3.9	13.6	-19.5	
IV	6.0	-	-	-	4.5	1.5	6.0	-	-	5.0	4.2	16.0	-19.2	6.0	-	5.0	4.2	16.0	-19.2	
V	6.0	-	-	-	4.6	1.4	6.0	-	-	6.9	3.3	17.5	-21.8	6.0	-	6.9	3.3	17.5	-21.8	
VI	6.0	-	-	-	5.2	0.8	6.0	-	-	7.1	3.7	14.7	-19.5	6.0	-	7.1	3.7	14.7	-19.5	
VII	6.0	335.0	-	-	5.5	335.5	6.0	335.0	335.0	54.7	34.6	14.1	237.6	6.0	335.0	54.7	34.6	14.1	237.6	
VIII	6.0	-	-	-	6.2	-0.2	6.0	-	-	4.5	4.8	17.6	-20.9	6.0	-	4.5	4.8	17.6	-20.9	
IX	6.0	-	-	-	6.2	-0.2	6.0	-	-	4.5	1.6	13.8	-13.9	6.0	-	4.5	1.6	13.8	-13.9	
X	6.0	-	-	-	-	6.0	6.0	-	-	4.4	3.4	-	-1.8	6.0	-	4.4	3.4	-	-1.8	

Considering this, the lowest value of sulphur balance was determined in corn in treatment VI, with the difference between input and output of sulphur: $-35.5 \text{ kg ha}^{-1} \text{ S-SO}_4$, while the highest level was determined for soybean in treatment VII, where the difference between input and output of sulphur was $335.5 \text{ kg ha}^{-1} \text{ S-SO}_4$. These could be explained because of high water shortage in 2011, when precipitation was 44 % below average (Zgorelec et al., 2015), and as a result, there was no lysimeter or drainage leaching. Crops with low crop density (corn) had the highest losses through drainage (68.1 kg ha^{-1} – VII) and lysimeter (251.3 kg ha^{-1} – VII) water in comparison to crops with high crop density (winter wheat, soybean, oilseed rape).

Sulphur balance was analysed in the research of sulphate leaching in an organic crop rotation on sandy soil in Denmark, from 1994 to 1998. Considerable sulphate leaching occurred in the organic crop rotation, and it was equivalent to 60 % of the total input. The conclusion was that immediate sulphur deficiency may not occur, but negative sulphur balance must be expected in the long period (Eriksen, Askegaard 2000). A net negative total sulphur balance of 60 kg ha^{-1} for sorghum, 54 kg ha^{-1} for rice and 68 kg ha^{-1} for sugarcane, especially from non-sulphur applied plots were observed (Singh, 2014) in an experiment on sulphur balance in soils influenced by sulphur carriers and crops in India.

Conclusions

In this research, sulphur addition with FG, amelioration with zeolite tuff and CaCO_3 and fertilization with different nitrogen levels addresses important issues related to plant nutrition in especially intensive agriculture on less quality soil and the protection of the environment from pollution. Global S balance in the examined agroecosystem is in deficit except in the FG treatment. The results show that S application through FG is an acceptable and necessary measure for preventing soil degradation (in soils where S balance is in deficit in combination with calcification if soil pH is low). In this study S application resulted in 7.0 % increase of S soil amount, with losses of 6.7 % through lysimeter water, and 18.3 % through drainage water. Long-term FG application could be beneficial however it is necessary to determine the optimal dose of FG for each soil type, climatic conditions and crop, and to find sustainable amount that would increase sulphur content in soil and minimize S leaching because excessive FG application can lead to excessive accumulation of S in soil, which could risk surface water and groundwater loads.

References

- Akter, F., M. Nurul Islam, A. T. M. Shamsuddoha, M. S. I. Bhuiyan, S. Shilp, 2013. Effect of Phosphorus and Sulphur on Growth and Yield of Soybean (*Glycine Max L.*). *International Journal of Bio-resource and Stress Management*, 4, 556 – 561.
- Beeson, K.C., 1941. The mineral composition of crops with particular reference to the soils in which they were grown. A review and compilation. *Miscellaneous Publication*, 369, 1 – 164.
- Bytnerowicz, A., K. Omasa, E. Paoletti, 2007. Integrated effects of air pollution and climate change on forests: a northern hemisphere perspective. *Environmental Pollution*, 147, 438 – 445.

Camargo, J.A., A. Alonso, 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystem: a global assessment. *Environment International*, 32, 831 – 849.

Camberato, J., S. Maloney, S. Casteel, 2012. Sulfur deficiency in corn. Purdue University Department of Agronomy, Soil fertility update. Last update May 2012. URL: <http://www.kingcorn.org/news/timeless/SulfurDeficiency.pdf>.

Camberato, J., S. Casteel, 2017. Sulfur deficiency. Purdue University Department of Agronomy, Soil Fertility Update. Last update 11 July 2017. URL: <https://www.agry.purdue.edu/ext/corn/news/timeless/sulfurdeficiency.pdf>.

Eriksen, J., J. V. Mortensen, 1999. Soil sulphur status following long-term annual application of animal manure and mineral fertilizers. *Biology and Fertility of Soils*, 28, 416 – 421.

Eriksen, J., M. Askegaard, 2000. Sulphate leaching in an organic crop rotation on sandy soil in Denmark. *Agriculture, Ecosystems & Environment*, 78, 107–114.

Eriksen, J., J. E. Olesen, M. Askegaard, 2002. Sulphate leaching and sulphur balances of an organic cereal crop rotation on three Danish soils. *European Journal of Agronomy*, 17, 1 – 9.

Erismann, J.W., A. Vermeulen, A. Hensen, C. Flechard, U. Dammgren, D. Fowler, M. Sutton, L. Grunhage, J. P. Touvinen, 2005. Monitoring and modelling of biosphere/atmosphere exchange of gases and aerosols in Europe. *Environmental pollution*, 133, 403 – 413.

Fagerli, H., W. Aas, 2008. Trends of nitrogen in air and precipitation: Model results and observations at EMEP sites in Europe, 1980 – 2003. *Environmental pollution*, 154, 448 – 461.

Food and agriculture organization of the United Nations – FAO. (2006). World reference base (WRB) for soil resources, a framework for international classification, correlation and communication, Rome. Last update: 31 October 2018. URL: <http://www.fao.org/faostat/en/#home>.

Förster, S., G. Welp, H. Scherer, 2009. Sulphur speciation in bulk soil and different aggregate fractions as influenced by longterm application of organic fertilizers. *Plant Soil Environment*, 58, 316 – 321.

Giannitrapani, M., A. Bowman, M. Scott, R. Smith, 2006. Sulphur dioxide in Europe: Statistical relationships between emissions and measured concentrations. *Atmospheric Environment*, 40, 2524 – 2532.

Gupta, R.K., S. K. Dubey, 1998. Sulphur management in rainfed cropping systems in Madhya Pradesh. *Fert. News*, 43, 57 – 60, 63 – 67.

Györi, Z., 2005. Sulphur content of winter wheat grain in long term field experiments. *Communications in Soil Science and Plant Analysis*, 36, 373 – 382.

HGCA, 1998. Sulphur requirements of oilseed rape, Topic Sheet No. 12. URL: <http://adlib.everysite.co.uk/resources/000/100/265/TS12.pdf>.

HRN EN ISO 10304-1, 1998. Water quality - Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions – Part 1: Method for water with low contamination.

Croatian Standards Institute. URL: <http://31.45.242.218/HZN/todb.nsf/wFrameset2?OpenFrameSet&Frame=Down&Src=%2FHZN%2Ftodb.nsf%2FNormaSve%2F26ecbec7e0091709c1257591004525ac%3FOpenDocument%26AutoFramed>.

HRN EN ISO 10381-1 to 8, 2002-2006. Soil quality - Sampling - Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination.

- Croatian Standards Institute. URL:
<http://31.45.242.218/HZN/Todb.nsf/wFrameset?OpenFrameSet&Frame=Down&Src=%2FHZN%2FTodb.nsf%2F66011c0bda2bd4dfc1256cf300764c2d%2F3bc0070a8008469dc1256e3c003fb10a%3FOpenDocument%26AutoFramed> .
- HRN EN ISO 10390, 2005. Soil quality - Determination of pH.
- Croatian Standards Institute. URL:
<http://31.45.242.218/HZN/Todb.nsf/wFrameset?OpenFrameSet&Frame=Down&Src=%2FHZN%2FTodb.nsf%2F66011c0bda2bd4dfc1256cf300764c2d%2F0e782f7e2e6cb750c1256fbd002d42ec%3FOpenDocument%26AutoFramed> .
- HRN EN ISO 15178, 2005. Soil quality - Determination of total sulphur by dry combustion. Croatian Standards Institute. URL:
<http://31.45.242.218/HZN/Todb.nsf/wFrameset?OpenFrameSet&Frame=Down&Src=%2FHZN%2FTodb.nsf%2Fcd07510acb630f47c1256d2c006ec863%2Fc1256c8f003565d5c1256d29003da9c9%3FOpenDocument%26AutoFramed> .
- HRN EN ISO 11464, 2006. Soil quality - Pretreatment of samples for physico-chemical analysis. Croatian Standards Institute. URL:
<http://31.45.242.218/HZN/Todb.nsf/wFrameset?OpenFrameSet&Frame=Down&Src=%2FHZN%2FTodb.nsf%2Fcd07510acb630f47c1256d2c006ec863%2F6a1dc151c271f96bc1257443002ee854%3FOpenDocument%26AutoFramed> .
- Hu, Z. Y., F. J. Zhao, S. P. McGrath, 2005. Sulphur fractionation in calcareous soils and bioavailability to plants. *Plant Soil*, 268, 103 – 109.
- Husnjak, S., 2014. Croatian soil systematics. *Hrvatska sveucilisna naklada*, Zagreb, Croatia, 373. (in Croatian)
- Isaac, R.A., J. D. Kerber, 1971. Atomic absorption and flame photometry: Techniques and uses in soil, plant and water analysis. In: Walsh LM, editor, *Instrumental methods for analysis of soil and plant tissue*. Madison (WI): ASA-CSSA-SSSA, 18 – 37.
- ISO 24333, 2009. Cereals and cereal products – Sampling. International Organization for Standardization. URL: <https://www.iso.org/standard/42165.html>
- Janzen, H.H., B. H. Ellert, 1998. Sulfur dynamics in cultivated, temperate agroecosystems. In D.G. Maynard (Ed), *Sulphur in the Environment*, New York, 11 – 43.
- Knights, J.S., F. J. Zhao, B. Spiro, S. P. McGrath, 2000. Long-term effects of land use and fertilizer treatment on sulfur cycling. *Journal of Environmental Quality Abstract*, 29, 1867 – 1874.
- Kotkova, B., J. Balik, J. Cerny, M. Kulkanek, M. Bazalova, 2008. Crop influence on mobile sulphur content and arylsulphatase activity in the plant rhizosphere. *Plant soil environment*, 54, 100 – 107.
- Lamond, R.E., 1997. Sulphur in Kansas: Plant, Soil, and Fertilizer Considerations. Kansas State University Cooperative Extension Bulletin. *Soil Fertility*, URL: <https://www.bookstore.ksre.ksu.edu/pubs/MF2264.pdf>
- McGrath, S.P., 2003. Sulphur: A secondary nutrient? Not anymore! *New AG International*, March, 70 – 76.
- Monaghan, R. M., R. J. Paton, L. Smith, C. Binet, 2000. Nutrient losses in drainage and surface runoff from a cattle-grazed pasture in Southland. *Proceedings of the New Zealand Grassland Association*, 62, 99 – 104.
- Sahota, T.S., 2006. Importance of Sulphur in Crop Production. *Biogeochemistry*, 1, 45 – 62.
- Salvagiotti, F., J. M. Castellarin, D. J. Miralles, H. M. Pedrol, 2009. Sulfur fertilization improves nitrogen use efficiency in wheat by increasing nitrogen uptake, *Field Crops Research*, 113, 170 – 177.

- Sawyer, E.J., W. D. Barker, 2002. Sulfur application to corn and soybean crops in Iowa, Department of Agronomy, Iowa State University. URL: <http://www.agronext.iastate.edu/soilfertility/info/sulfuricm02.pdf>
- Sestak, I., M. Mesic, Z. Zgorelec, I. Kistic, F. Basic, 2014. Winter wheat agronomic traits and nitrate leaching under variable nitrogen fertilization. *Plant Soil Environment*, 60, 394 – 400.
- Singh, P.S., P. M. Singh, 2014. Effect of Sulphur Fertilization on Sulphur Balance in Soil and Productivity of Wheat in Wheat-Rice Cropping System. *Agricultural Research*, 3, 284 - 292.
- Skoric, A., 1986. Genesis, Development and Taxonomy of Soil. University of Zagreb, Zagreb, Croatia. (in Croatian)
- Statistical Yearbook of the Republic of Croatia, 2002: 54; 2003: 55; 2004: 55; 2005: 56; 2006: 57; 2007:56; 2008; 2009: 50; 2010: 50 ;2011: 50 ;2012: 50; 2013: 50; 2014: 56. URL: https://www.dzs.hr/eng/publication/stat_year.htm
- Sullivan, T.J., B. J. Cosby, K. A. Tonnessen, D. W. Clow, 2005. Surface water acidification responses and critical loads of sulfur and nitrogen deposition in Loch Vale watershed, Colorado. *Water Resources Research*, 41, 1 – 15.
- Tandon, H.L.S., 2011. Sulphur in soils, crops & Fertilisers from research to practical application. Fertiliser Development and Consultation Organisation, New Delhi, India.
- Tiwari, K.N., B. R. Gupta, 2006. Sulphur for sustaining high yield agriculture in Uttar Pradesh. *IJF*, 37 – 52.
- Vukovic, I., M. Mesic, Z. Zgorelec, A. Jurisic, K. Sajko, 2008. Nitrogen use efficiency in winter wheat. *Alps-Adria Scientific Workshop*, Stara Lesna, Slovakia, 36, 1199 – 1202.
- Vyshpolsky, F., K. Mukhamedjanov, U. Bekbaev, S. Ibatullin, T. Yuldashev, A. D. Noble, A. Mirzabaev, A. Aw-Hassand, M. Qadir, 2010. Optimizing the rate and timing of phosphogypsum application to magnesium-affected soils for crop yield and water productivity enhancement. *Agricultural Water Management*, 97, 1277 – 1286.
- Walaszek, K., M. Kryza, A. J. Dore, 2013. The impact of precipitation on wet deposition of sulphur and nitrogen compounds, *Ecological Chemistry and Engineering*, 20, 733 – 745.
- Yang, Z., B. R. Singh, S. Hansen, Z. Hu, H. Riley, 2007. Aggregate associated sulfur fractions in long-term (>80 years) fertilized soils. *Soil Science Society of America Journal*, 71, 163 – 170.
- Zgorelec, Z., G. Pehcec, F. Basic, I. Kistic, M. Mesic, S. Zuzul, A. Jurisic, I. Sestak, V. Vadic, M. Cackovic, 2012. Sulphur cycling between terrestrial agroecosystem and atmosphere. *Archives of Industrial Hygiene and Toxicology*, 63, 301 – 310.
- Zgorelec, Z., M. Mesic, I. Kistic, D. Bilandzija, A. Jurisic, F. Basic, I. Sestak, I. Bogunovic, 2015. Influence of Different Land Management on Climate Change. 2nd International Symposium for Agriculture and Food - ISAF 2015, 266 – 266.
- Zhao, Y., L. Duan, J. Xing, T. Larssen, C. P. Nielsen, J. Hao, 2009. Soil acidification in China: is controlling SO₂ emissions enough? *Environmental Science and Technology*, 43, 8021 – 8026.



Soil Enzymes Assessment Around Amega Cement Factory in Nigeria.

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Abstract

High soil quality is important for agricultural activities but pollution from cement industries is of great threat to sustainable agriculture in Nigeria. The aim of this study is to assess the effect of heavy metals in cement dust on the soil enzymes activities.

This study investigated the activities of some selected soil enzymes, the microbial communities' population, the concentrations of some heavy metals, some selected soil macronutrients and the physico-chemical properties (pH, moisture, and temperature) of the soil surface (0-15 cm), within the vicinity of a cement factory in Nigeria.

The pH, total organic nitrogen (TON), total organic carbon (TOC) and heavy metals decreased with increasing distance from the cement factory. The microbial population around the factory was (34.00 ± 2.64 CFU g⁻¹) and (92.00 ± 1.00 CFU g⁻¹) at 100 m and the control site respectively. All the soil heavy metals contents analyzed are less than the permissible limit except Cd. Moreover, the enzyme activities increased away from cement factory except alkaline phosphatase that decreases with increase in distance. The enzymes activities (except alkaline phosphatase) correlated negatively with the content of all heavy metals, the pH, the TON, the TOC and temperature but positively correlated with moisture, phosphorous and microbial populations. The inverse correlations between most of the heavy metals, the pH and soil enzymes activities could be a result of the pollution. This means that the cement production exhibits a significant effect on the enzyme activities.

Key Words: anthropogenic impact, bioaccumulation and biomagnification, geomagnification, soil enzymes, xenobiotics.

Introduction

The biophysical environment contains definite amount of elements and compounds in a given proportion by nature and is considered polluted when there is an imbalance in the natural composition of all these compounds. The toxic metals, from the xenobiotics, entering the ecosystem may lead to geoaccumulation, bioaccumulation and biomagnifications in organisms in the environment (Ogunkunle and Fatoba, 2014).

The xenobiotics can be released intentionally into the soil or dispersed by wind and rain to a far distance from the source of pollution. The concentrations of xenobiotics in soils are associated with biological and geochemical cycles and are influenced by anthropogenic activities, such as transport, waste disposal, industrialization, social and agricultural activities. They have an effect on environmental pollution and the global ecosystem.

One industry that emits pollutants in the form of dust and gases which find their way into the soil is the cement industry (Addo, 2013). Dust from cement and other factories leads to considerable change in pH and accumulation of metals in the soil which may affect both the composition and physiological processes of microorganisms leading to a reduction in microbial biomass and enzyme activities (Utobo and Tewari, 2014).

Soil enzymes are a group of enzymes that inhabits the soil and are continuously playing an important role in maintaining the soil biological, physical and chemical properties, fertility, and soil health (Das and Varma, 2011). All soils contain a group of enzymes that determine the soil metabolic processes (Baldrian, 2009) which in turn, depend on its physical, chemical, microbiological, and biochemical properties.

Some of the soil enzymes including amylase, b-glucosidase, cellulose, chitinase, dehydrogenase, phosphatase, protease, and urease are released from plants and animals, organic compounds, and microorganisms in the soil. Soil enzymes are the mediators and catalysts of important soil functions and have a crucial role in carbon (β -glucosidase and β -galactosidase), nitrogen (urease), phosphorus (phosphatase), and sulphur (sulphatase) cycle (Karaca *et al.*, 2011).

The importance of soil as an ecosystem cannot be underestimated. It serves as reservoir to a lot of nutrients and minerals which are essential for plant growth. However, soils around Lafarge cement factory in Sagamu are under threat of serious degradation as a result of cement dust deposition. It is therefore important to assess the level of degradation for the purpose of conservation of biodiversity and protection of ecosystem around the factory.

Also, to the best of our understanding, no work till date has reported the use of soil enzymes around Lafarge cement factory. Therefore, it is very important to assess the level of soil pollution around the study area using the enzyme activities, because the knowledge can be used as bioindicator of ecosystem perturbation, agricultural practices and xenobiotic pollution.

The aim of this study is to assess the effect of heavy metals in cement dust on soil enzymes activities around Lafarge cement factory in Sagamu, Sagamu Local Government Area, Ogun state, Nigeria.

Materials and Methods

The Study Area

The study was carried out in the Lafarge cement factory which is situated in Sagamu, southwest Nigeria ($6^{\circ}50' 7^{\circ}00' \text{ N}$; $3^{\circ}45' 4^{\circ}00' \text{ E}$). The factory is located 72 km southeast of Ibadan (largest city in West Africa), 32 km west of Ijebu Ode, 63 km southeast of Abeokuta and 67 km northwest of Lagos. The factory was established, commissioned and became fully operational in 1978 with the present production capacity of 900 000 tonnes/year (Lafarge Cement WAPCO PLC, 2011). The area is characterized by high annual temperature, high rainfall, high evapotranspiration and high relative humidity which make it to be classified as humid tropical region (Ogunkunle and Fatoba, 2014). The soil type of Shagamu is Ferralitic and Ferruginous (Ilalokhoin *et al.*, 2013). The climate is classified as humid tropical climatic zone and controlled by the Tropical Maritime and Tropical Continental air masses (Ilalokhoin *et al.*, 2013). The mean annual rainfall of Shagamu for 2015 was 1 100 mm (NIMET, 2015).



Figure 1. Google map of Lafarge factory

Collection of Samples

Sampling was carried out in the wet seasons of 2015 in the area surrounding the factory excluding the northern part of the factory because of the presence of swamps. At each sampling location, three subsamples were collected at the depth of 0 – 15 cm within 10 m radius of a point using a soil auger. The samples were bulked together to obtain a composite sample and recorded against the coordinate position. A total of 15 composite topsoil samples were collected in the west, the south and the east parts at 100 m, 200 m, 300 m, 500 m and 1000 m distance from the

factory respectively. The coordinates at every sampling points were taken by a hand-held GPS (Garmin 2H).

Control samples were collected at a distance of about 15 km from the cement factory where there was no record of cement dust pollution. The soil samples collected were placed in polyethylene bags, properly labeled and transported to the laboratory. Before chemical analysis in the laboratory, the soil samples were air-dried, sieved through a 2-mm sieve mesh to remove coarse material and debris, and pulverized into powder. The soil was transferred to the storage room and was stored at 30 °C until the time of analysis. Microbial and enzyme analysis were done within 24 to 48 h.

Soil Physico-Chemical Analysis

The soil pH was measured in a soil water suspension (1 : 2, soil : water) using glass electrode and temperature was also measured by soil thermometer (Frederick *et al.*, 2014) while the moisture content was determined gravimetrically after drying at 105 °C according to AOAC (2005). The following soil nutrients were selected and analyzed as follows: total organic carbon was determined based on modified Walkley-Black chromic acid wet oxidation method according to Sato *et al.* (2014). Total phosphorus (TP) was determined according to Adesanwo *et al.* (2013). Total nitrogen was determined by Kjeldahl method according to AOAC (2005).

Heavy Metal Analysis in Soil

The soil samples (air-dried and digested) were analyzed for heavy metals content using Peking Elmer Model 403 atomic absorption spectrophotometer (AAS) according to AOAC (2005) after nitric acid digestion of the soil. The heavy metals studied were copper (Cu), cobalt (Co), lead (Pb), manganese (Mn), cadmium (Cd), nickel (Ni) and zinc (Zn). In addition, calcium (Ca) and aluminum (Al) content of the soil samples were also analyzed because they are one of the main constituent elements in the cement.

Enzymatic Analysis and Microbial Population in Soil

Enzyme substrates were purchased from Sigma-Aldrich Inc., England. Enzyme activities were measured according increase of resultant or decrease of substrate by colorimetric determination methods. Soil urease, acid phosphatase, alkaline phosphatase and dehydrogenase were determined according to Ofoegbu *et al.* (2013). β -glucosidase activity was determined according to Ramamoorthy (2015) and Zhang (2010). Soil invertase activity was determined according to the method described by Frankenberger Jr. and Johanson (1983) cited by Effron *et al.* (2004). Cellulase activity was measured with a method adapted from the one described by Alef and Nannipieri (1995). The method employed for determining soil amylase activity was essentially based on starch hydrolysis according to Khan *et al.* (2007).

Also, the number of microbial population was determined by the method of serial dilutions (Kulandaivel *et al.*, 2015). Soil samples were subjected to serial dilution and spread on

nutrient agar plates and potato agar plates, incubated for 48 h to grow the microbial colonies proper. Colony forming units were counted by colony counter.

Statistical Analysis

Data were subjected to two-way Analysis of Variance (ANOVA) and Dunnett's multiple comparison tests at $p \leq 0.05$ probability level using Statistical Package for the Social Sciences (SPSS) version 20. Spearman correlation analysis was also employed to determine the relationships existing among the heavy metals content, the pH, the microbial population, enzyme activities and soil nutrient contents.

Results and Discussion

The results from the Analysis of Variance (ANOVA) showed that there were significance mean differences at ($p < 0.05$) between the soil samples taken at various distances and the control sample for all the enzyme activities, heavy metals; the soil nutrients except total organic nitrogen ($f = 0.18$), the soil physiochemical properties except pH values and lastly significant for all the microbial population constituents. Fang *et al.* (2017) analyzed the activity of a number of enzymes, in three types of land (farmland, woodland, and grassland) to evaluate soil pollution by heavy metals (Pb, Zn, and Cd). Their results showed that urease was the most sensitive enzyme to heavy metal pollution in the farmland. This is in agreement with our results where urease had the lowest enzyme activities (at 100 m). Caravaca *et al.* (2017) also reported that Urease activity was only decreased in the zone nearest to cement factory; and glucosidase activities declined significantly with decreasing distance to the cement factory in comparison with that in the unaffected zone which is in agreement with our work. Furthermore, Chen *et al.* (2017) reported that the soil moisture, contents of silt and total nitrogen were the most important variables responsible for soil extracellular enzyme activity variation.

Enzyme activities and the physicochemical properties of the soil

There was significant difference ($p < 0.05$) in soil enzymatic activities with respect to the distance from the factory except alkaline phosphatase. This implies that the enzymatic inhibition could originate from the factory (cement dust). The highest activity was recorded for invertase ($517.33 \pm 2.08 \mu\text{g g}^{-1}$) at the control site while the lowest activity was recorded for urease ($0.14 \pm 0.03 \mu\text{g g}^{-1}$) at 100 m distance respectively. The enzyme inhibition could be attributed to the binding of the heavy metals at the active site of the enzymes which could subsequently inhibit their catalysis. According to Poli *et al.* (2009) heavy metals is a strong enzyme inhibitors.

The pH range between 6.62 ± 0.10 (at the control) to 10.77 ± 0.81 (at 100 m) indicated that the factory soil was alkaline. The alkalinity was due to deposition and liming by calcium ion (Ca^{2+}) from cement dust. Invertase had the highest enzymatic activity ($517.33 \pm 2.08 \mu\text{g g}^{-1}$) at pH of 6.62 ± 0.10 (at the control) while the lowest value was recorded for urease ($0.14 \pm 0.03 \mu\text{g g}^{-1}$) at pH of 10.77 ± 0.81 . This may be as a result of higher sensitivity of urease to alkaline pH as similarly reported by Frederick *et al.* (2014). Generally, the lower enzymes activities could be

due high pH around the factory as most of these enzymes could only function optimally at lower pH except alkaline phosphatase.

Table 1. The relationship between the enzyme activity and the sampling distance from different locations

Enzyme ($\mu\text{g g}^{-1}$)	Distance - radius (m)					
	100	200	300	500	1000	15000
URS	0.14 $\pm$ 0.03	0.21 $\pm$ 0.04	0.30 $\pm$ 0.06	0.37 $\pm$ 0.06	0.48 $\pm$ 0.08	0.97 $\pm$ 0.01
ALP	68.67 $\pm$ 4.16	52.67 $\pm$ 5.03	57.67 $\pm$ 4.04	54.33 $\pm$ 2.08	32.67 $\pm$ 1.57	26.67 $\pm$ 0.58
ACP	101.33 $\pm$ 3.06	114.67 $\pm$ 4.16	134.33 $\pm$ 5.51	145.00 $\pm$ 4.00	163.00 $\pm$ 5.00	177.67 $\pm$ 1.53
BGLU	2.47 $\pm$ 0.38	5.17 $\pm$ 0.25	6.74 $\pm$ 0.31	7.83 $\pm$ 0.25	9.27 $\pm$ 0.32	11.23 $\pm$ 0.25
DHA	1.60 $\pm$ 0.3	2.27 $\pm$ 0.60	3.0 $\pm$ 0.79	3.63 $\pm$ 0.75	4.5 $\pm$ 1.10	7.77 $\pm$ 0.15
INVS	120.67 $\pm$ 22.75	156.33 $\pm$ 20.40	212.33 $\pm$ 36.67	268.33 $\pm$ 69.40	349 $\pm$ 66.26	517.33 $\pm$ 2.08
CLS	17.67 $\pm$ 3.06	23.00 $\pm$ 4.58	28.67 $\pm$ 4.50	33.33 $\pm$ 3.51	40.67 $\pm$ 3.51	65 $\pm$ 2.64
AMY	4.71 $\pm$ 0.95	6.21 $\pm$ 1.73	7.49 $\pm$ 1.48	8.76 $\pm$ 1.19	10.78 $\pm$ 0.58	12.17 $\pm$ 0.12

Values are mean $\pm$ standard error of triplicate values.

KEY: Urease (URS) ($\mu\text{g N-urea g}^{-1}$ dry soil 5h^{-1}), Alkaline phosphatase (ALP) ($\mu\text{g p-nitrofenol g}^{-1}$ dry soil h^{-1}), Acid phosphatase (ACP) ($\mu\text{g p-nitrofenol g}^{-1}$ dry soil h^{-1}), B-glucosidase (BGLU) ($\mu\text{g p-nitrofenol g}^{-1}$ dry soil h^{-1}), Dehydrogenase (DHA) ($\mu\text{g triphenylformazan g}^{-1}$ dry soil 24h^{-1}), Invertase (INVS) ($\mu\text{g reducing sugar g}^{-1}$ dry soil 24h^{-1}), Cellulase (CLS) ($\mu\text{g glucose g}^{-1}$ dry soil 24h^{-1}), Amylase (AMY) ($\mu\text{g starch degraded g}^{-1}$ dry soil 2.5h^{-1}).

The study showed that the soil pH around factory was positively correlated for alkaline phosphatase while it was negatively correlated with all other enzymes, because the enzyme requires alkaline pH for optimal activity. This is in agreement with the work of Karaca *et al.* (2011) and Caravaca *et al.* (2017).

Also, there were positive correlations between the soil moisture content and the enzymes activities. This showed that moisture is required for optimum enzyme activity (through high microbial activities) in the soil. Also, high moisture has been predicted to support high microbial activities in the soil (Ahmed *et al.*, 2018).

There was significance difference ($p < 0.05$) between the mean values of the pH, soil moisture (except the temperature) and the enzyme activities at different sampling sites compared with the control samples.

The heavy metals, Calcium, Aluminum and the enzyme activities

The heavy metal concentrations decrease with increasing distance from the factory. The lowest concentration was observed at the control soil sample (15000 m) except zinc. The concentration of zinc at the control site (15.32 mg kg^{-1}) was higher than the concentrations of Zn around the factory. There were statistically significant variations in the concentrations of Cu, Pb, Mn, Cd, Ni, Co, Zn, Al and Ca at some distances, when compared to the control samples ($p < 0.05$). This implied that heavy metals are from the cement dust pollution. Moreover, Ca has the highest concentration at all sampling points which are also all statistically significant to the control and could be the main contributor to soil pollution in the environment. This is because Ca is an important element in the cement kiln process.

Dunnett's Multiple Comparison tests also revealed further that for Cu and Mn, there were no significant differences in the mean soil samples at 500 m, 1000 m compared to the control. Cadmium showed significant differences at different locations except at 1000 m only. We reported previously that Zn showed no significant difference at 200 m, 300 m, 500 m and 1000 m compared to the control and Al at 1000 m to the control samples (Oludoye and Ogunyebi, 2017).

There were also negative correlations between the enzyme activities and heavy metal concentrations around the factory except the alkaline phosphatase that was positively correlated. Heavy metals have been reported to inhibit enzymes singly or in combination by synergism (Frederick *et al.*, 2014). Therefore, this implied that some of these metals might inhibit the activities of all the enzymes studied except alkaline phosphatase activities which are also in accordance with the work of Das and Varma (2011).

In order to determine the magnitude of the pollution, the heavy metals content was compared with Nigeria Federal Environmental Protection Agency (FEPA) maximum permissible concentration (MPC) for soil. It was observed that the concentrations of all the heavy metals except cadmium are within the MPC of FEPA. The soil Cd concentration is higher than the MPC at all distances except at the control. This shows that Cd concentration is very high around the cement factory. Cadmium is one of the trace elements found in raw mill and coal which are used in the formation of clinker (the most important constituent of cement) (Cipurkovic *et al.*, 2014). This high Cd concentration is unhealthy for the environment and human health because there are some farming activities currently going on in the vicinity of the cement factory. Cadmium could subsequently enter the food chains through the crops from the farms.

Table 2. FEPA and WHO maximum permissible concentrations for soil

Heavy metals	WHO limit (mg/kg)	FEPA limit (mg/kg)
Zn	50	300-400
Cu	36	70-80
Pb	85	1.6
Cd	0.8	3.0
Mn	Not fixed	Not fixed

Ni	35	18
Co	Not fixed	20

However, it is not only cement production that could release Cd into the environment but geologic processes (ferratillisation) could also contribute to the high concentration around the factory. It was also reported that high soil pH caused by limestone deposition (a component of cement) could immobilize Cd in the soil (Yun and Yu, 2015). Furthermore, Kim (2014) reported that Cd is maximally adsorbed at high pH and high temperature which significantly affected the adsorption capacity in alkaline soil.

Table 3. The mean value of heavy metal concentrations in the soil around the factory

Heavy metal (mg kg ⁻¹)	Average distance - radius (m) from east, west and south part of the factory					
	100	200	300	500	1000	15000
Cu	6.52 ± 0.80	5.69 ± 0.50	4.62 ± 0.79	3.71 ± 0.58	3.04 ± 0.53	2.16 ± 0.02
Pb	1.34 ± 0.06	1.24 ± 0.07	1.14 ± 0.09	1.06 ± 0.08	0.96 ± 0.09	0.27 ± 0.01
Cd	9.27 ± 0.42	8.63 ± 0.55	7.58 ± 0.44	6.60 ± 0.59	5.7 ± 0.42	2.56 ± 0.09
Mn	9.87 ± 0.19	9.25 ± 0.24	8.42 ± 0.49	8.00 ± 0.36	7.38 ± 0.27	6.77 ± 0.04
Ni	3.52 ± 0.09	3.30 ± 0.25	3.16 ± 0.21	2.97 ± 0.17	2.86 ± 0.16	2.09 ± 0.07
Co	16.97 ± 0.72	16.22 ± 0.61	15.05 ± 0.42	14.14 ± 0.54	13.74 ± 0.81	10.48 ± 0.10
Zn	17.25 ± 0.21	16.68 ± 0.26	16.15 ± 0.37	15.47 ± 0.70	14.71 ± 0.54	15.32 ± 0.25

Values are mean ± standard error of triplicate values

Table 4. The mean value of Ca and Al concentrations in the soil around the factory

Metal (mg kg ⁻¹)	Average distance - radius (m) from east, west and south part of the factory					
	100	200	300	500	1000	15000
Ca	201.05 ± 12.0	160.92 ± 11.08	144.02 ± 11.58	133.80 ± 9.86	97.06 ± 1.53	84.13 ± 0.26
Al	4.15 ± 0.06	3.65 ± 0.34	3.17 ± 0.32	2.53 ± 0.45	2.13 ± 0.17	1.81 ± 0.03

The soil nutrients analysis

There was decrease in the concentration of available phosphorus at various distances which showed a significant mean difference to the control at 15000 m. This can attributed to the precipitation of phosphorus into calcium phosphate at high pH (Cao *et al.*, 2007) while there was gradual decrease in the total organic carbon and nitrogen content of the soil from the factory to the control site, respectively.

Dunnett's Multiple Comparison tests showed that for there were no significant differences between the means for all the soil samples taken at varying distances and the control sample, for

organic nitrogen. In addition, there was no significant mean difference at 300 m, 500 m and 1000 m for total organic carbon.

Table 5. The mean values of selected soil nutrients with respect to distance

Distance (m)	Phosphorous (part per million)	Nitrogen (mg kg ⁻¹)	Carbon (%)
100	21.43 ± 2.59	178.00 ± 4.00	14.27 ± 1.02
200	24.57 ± 2.61	164.00 ± 4.00	12.53 ± 2.06
300	27.60 ± 3.53	144.00 ± 3.00	9.44 ± 0.70
500	29.47 ± 3.19	133.00 ± 3.00	7.59 ± 0.78
1000	31.03 ± 2.06	110.00 ± 2.00	6.72 ± 0.44
Control	58.30 ± 0.18	98.00 ± 4.00	6.30 ± 0.20

Values are mean ± standard error of triplicate values.

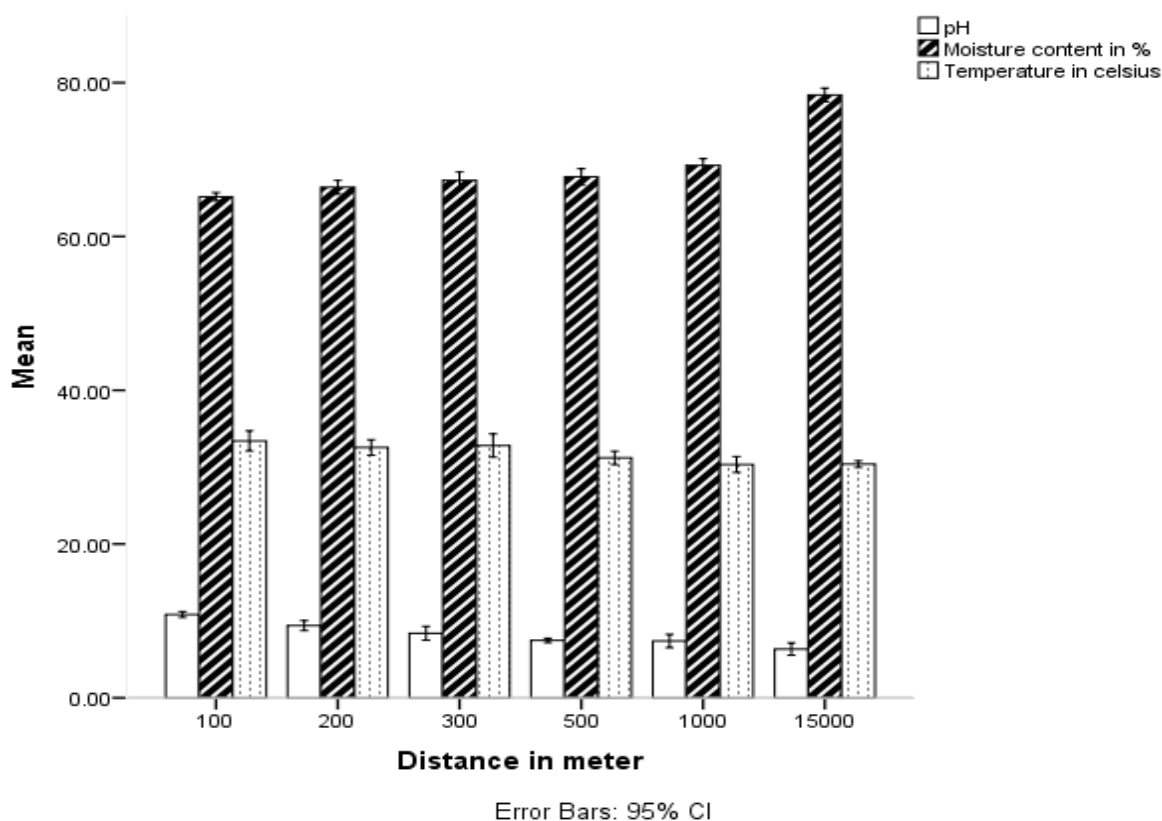


Figure 2. The relationship between the pH, moisture, and temperature with respect to distance

Soil microbial population

The microbial communities of the soil studied were significantly affected as a result of cement dust deposition. The result showed that the microbial communities of the control were statistically significantly higher ($p < 0.05$) than the polluted soil around the factory, which is in agreement with the work of Kulandaivel *et al.* (2015). Also, Caracava *et al.* (2017) reported that the prolonged exposure of soil to cement dust could result in shifts in the soil microbial function. This could also be attributed to the decrease in microbial biomass due to reduced enzymes activity. Spearman correlation analysis revealed that there was positive correlation between the microbial communities and the enzyme activities. This implied that enzymes are primarily derived from microorganisms but can also originate from plants and animals. Hence, factors affecting microbial activities will invariably affect soil enzymes. Moreover, the microbial count is also negatively correlated with the soil pH. This could be due to the fact that some of the microbes could not survive in alkaline conditions as this could affect the osmotic balance of their cells and consequently, cause reduction in their cell biomass.

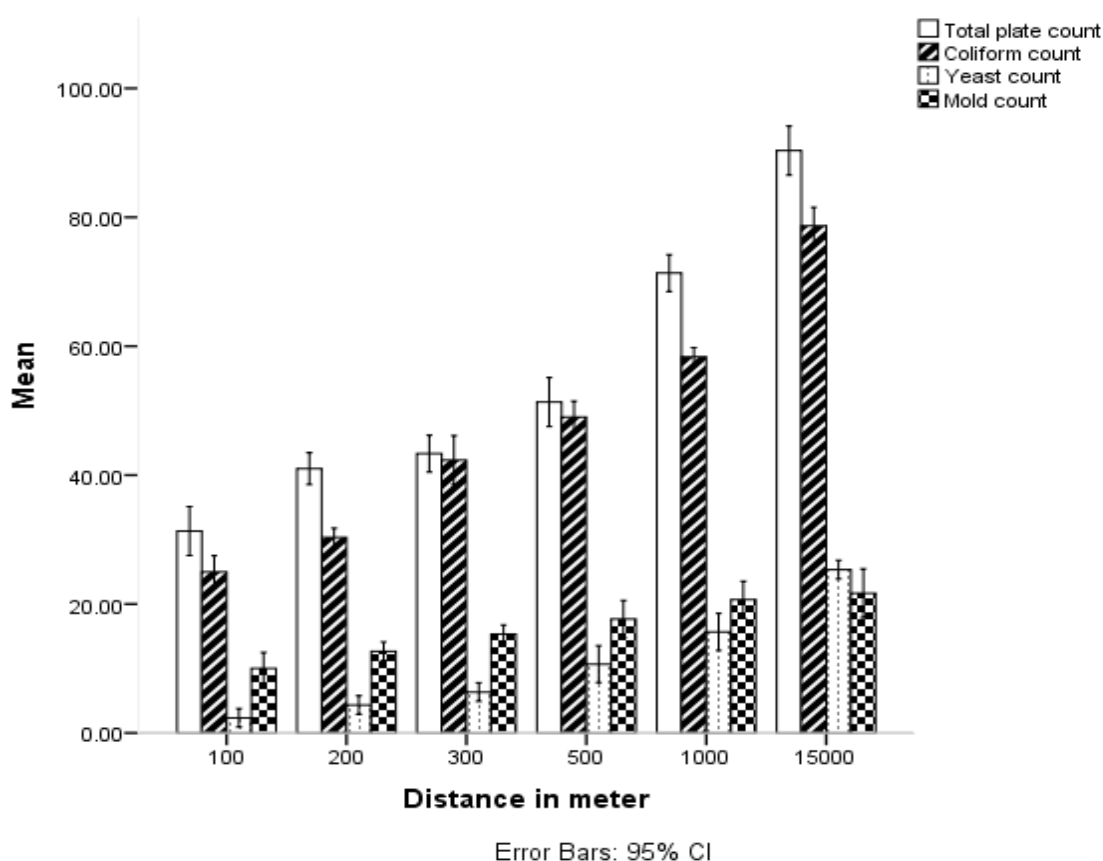


Figure 3. The relationship of microbial population from different soil samples with respect to distance from the factory.

Table 6. The Spearman's correlation coefficient among the enzyme activities and the heavy metal concentrations

	Cu	Pb	Cd	Mn	Ni	Co	Zn	Ca
Urease	-0.888	-0.900*	-0.918*	-0.892*	-0.994**	-0.984**	-0.669**	-0.863*
ALP	0.893*	0.856	0.910*	0.903**	0.888*	0.877**	0.824*	0.894**
ACP	-0.997*	-0.875*	-0.997	-0.999**	-0.928**	-0.951**	-0.921**	-0.992**
BGLU	-0.978*	-0.880**	-0.980**	-0.973	-0.985**	-0.943**	-0.899**	-0.989**
DHA	-0.950**	-0.970*	-0.972**	-0.952**	-0.988	-0.990**	-0.791**	-0.935**
Invertase	-0.950**	-0.970**	-0.972**	-0.952**	-0.988**	-0.990	-0.791**	-0.935**
Cellulase	-0.922**	-0.990*	-0.945**	-0.923**	-0.997**	-0.992**	-0.728	-0.900**
Amylase	-0.992*	-0.884**	-0.996**	-0.993**	-0.935**	-0.951**	-0.917**	-0.990

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Conclusion

All the heavy metals content of soil around the cement factory are below the MPC of FEPA except cadmium. The high Cd content could have emanated from the factory cement dust because cadmium is one of the trace elements in the fuel that is used for kiln production. Also, soil geologic processes and high pH around the factory could also result in Cd immobilization in the soil. Moreover, there is low nutrients content (phosphorus), low microbial population and high pH within the vicinity of the cement factory. All these factors had a significant adverse effect on and are inversely correlated with the soil enzymes. This indicates the ability of soil enzymes early soil pollution signal (or indicator) despite the permissible level of heavy metals (except cadmium).

The heavy metals content (especially cadmium) in the top soil (0-15 cm) is within the reach of plant roots and could have negative effects on the natives who are already using the sites around the factory as agricultural farms for planting food crops such as sugar cane, cassava, banana and maize respectively.

Therefore, there should be comprehensive ecological risk assessment of the soil ecosystem around the factory. In addition, human health risk assessment should be carried out to determine carcinogenic and non-carcinogenic risk through dietary exposure to some of these heavy metals (especially cadmium). This would help prevent the pollutants (heavy metals) from entering the food chain and help reduce the exposure of the inhabitants and the farmers. Also, farming activities should be totally discouraged around the factory.

Reference

Addo, M.A., Darko, E.O., Gordon, C., Nyarko, B.J.B., Gbadago, J.K., Nyarko, E., Affum, H.A., Botwe, B.O., 2012. Evaluation of heavy metals contamination of soil and vegetation in the vicinity of a cement factory in the Volta region, Ghana. *International Journal of Science and Technology* 2(1): 40–50.

Adesanwo, O. O., Ige, D. V., Thibault, L., Flaten D., Akinremi, W. 2013. Comparison of Colorimetric and ICP Methods of Phosphorus Determination in Soil Extracts. *Communications in Soil Science and Plant Analysis* 44(21): 3061-3075. Doi: <https://doi.org/10.1080/00103624.2013.832771>.

Ahmed, M. A., Sanaullah, M., Blagodatskaya, E., Mason-Jones, K., Jawad, H., Kuzyakov, Y., Dippold, M. A. 2018. Soil microorganisms exhibit enzymatic and priming response to root mucilage under drought. *Soil Biology & Biochemistry* 116: 410-418. Doi: <https://doi.org/10.1016/j.soilbio.2017.10.041>.

Alef, K., Nannipieri, P. 1995. Cellulase activity. In: Alef P (ed) *Methods in applied soil microbiology and biochemistry*. Academic Press, London, pp 382–384.

AOAC. 2005. *Official methods of analysis*. Association of official analytical chemists: Agricultural Chemicals; Contaminants; Drugs. 18th Ed. Association of Official Analytical Chemists Inc. Arlington, Virginia, USA.

Baldrian, P., 2009. Microbial enzyme-catalyzed processes in soils and their analysis. *Plant and Soil Environment* 55 (9): 370–378.

Bradford, M.M., 1976. A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein dye binding. *Analytical Biochemistry* 72(1-2): 248–254. Doi: [https://doi.org/10.1016/0003-2697\(76\)90527-3](https://doi.org/10.1016/0003-2697(76)90527-3).

Cao, X., Harris, W. G., Josan, M. S. and Nair, V. D., 2007. Inhibition of calcium phosphate precipitation under environmentally-relevant conditions. *Science of the Total Environment*. 383(1-3): 205-215.

Chen, H., Luo, P., Wen, L., Yang, L. Q., Wang, K. L., Li, D. J. 2017. Determinants of soil extracellular enzyme activity in a karst region, southwest China. *European Journal of Soil Biology* 80: 69-76. Doi: <https://doi.org/10.1016/j.ejsobi.2017.05.001> .

Das, S.K., Varma, A., 2011. Role of enzymes in maintaining soil health. In: In: Soil Enzymology, Soil Biology 22. Shukla, G., Varma, A. (Eds.). Springer-Verlag, Berlin Heidelberg, pp.25-42.

Cipurkovic, A., Trumic, I., Hodžic, Z. Selimbašic, V. and Djozic, A. (2014). Distribution of heavy metals in Portland cement production process. 5(6): 252-259.

Effron, D., de la Horra, A.M., Defrieri, R.L., Fontanive, V., Palma, P.M., 2004. Effect of cadmium, copper, and lead on different enzyme activities in a native forest soil. *Communication of Soil Science and Plant Analysis* 35(9-10): 1309–1321. Doi: <https://doi.org/10.1081/CSS-120037548> .

Egejuru, L.O., Akubugwo, E.I., Ude, V.C., Ugbogu, O.C., Ugbogu, A.E., 2014. Evaluation of physicochemical properties, microbial loads and enzymes activity studies of agrochemicals on the Imo-River basin farm in Imo State Nigeria. *International Journal of Current Microbiology and Applied Sciences* 3(2): 776-786.

Fang, L. C., Liu, Y. Q., Tian, H. X., Chen, H. S., Wang, Y. Q., Huang, M. 2017. Proper land use for heavy metal-polluted soil based on enzyme activity analysis around a Pb-Zn mine in Feng County, China. *Environmental Science and Pollution Research* 24(36): 28152-28164. Doi: <https://doi.org/10.1007/s11356-017-0308-4> .

Frankenberger Jr., W. T., Johanson, J. B., 1983. Method of measuring invertase activity in soils. *Plant and Soil* 74: 301-311.

Frederick, O.O., Iroha, A.E., Oswald, E.C., 2014. Evaluation of the concentration of selected heavy metals and the effects on soil enzymatic activities in an Abandoned Cement Factory in NigercemNkalagu and its environs. *International Journal of Biochemistry Research and Review* 4(1): 16-27. Doi: <https://doi.org/10.9734/IJBCRR/2014/5019> .

Ilalokhoin, P.O., Otaru, A.J., Odigure, J.O., Abdulkareem, A.S., Okafor, J.O., 2013. Environmental impact assessment of a proposed cement plant in southwestern Nigeria. *IOSRJournal of Environmental Science, Toxicology and Food Technology* 3(5): 83–99.

Karaca, A., Cema, C.C., Turgay, O.C., Kizilkaya, R., 2011. Soil enzymes as indicator of soil quality. In: Soil Enzymology, Soil Biology 22. Shukla, G., Varma, A. (Eds.). Springer-Verlag, Berlin Heidelberg, pp.119-148.

Khan, S., Cao, Q., Hesham, A.E., Xia, Y., He, J., 2007. Soil enzymatic activities and microbial community structure with different application rates of Cd and Pb. *Journal of Environmental Science* 19(7): 834–840. Doi: [https://doi.org/10.1016/S1001-0742\(07\)60139-9](https://doi.org/10.1016/S1001-0742(07)60139-9)

Kim, M. (2014). A study on the adsorption characteristics of cadmium and zinc onto acidic and alkaline soils. *Environmental Earth Sciences*. 72, (10): 3981–3990.

Kulandaivel, S., Nagarajan, S., Priyanga, A., Saravanapandian, R., Thangarani, A., 2015. Effect of cement dust pollution on microbial properties and alkaline phosphatase enzyme activity in soil. *International Journal of Current Microbiology and Applied Science* 4(2): 641-649.

Lafarge Cement WAPCO PLC. 2011. Lafarge WAPCO: Supporting Nigeria's development, Annual Report–Lafarge Cement WAPCO PLC. pp. 2–4 .

Nayak, D.C., Sen, T.K., Chamuah, G.S., Sehgal, J.L., 1996. Nature of soil acidity in some soils of Mainpur. *Journal of Indian Society of Soil Science* 44(2): 209-212.

Nelson, N. 1944. A photometric adaptation of the Somogyi method for determination of glucose. *Journal of Biological Chemistry* 153: 375–380.

NIMET. 2015. Seasonal rainfall prediction and socio–economic implications for Nigeria. Federal Government of Nigeria, Nigerian Meteorological Agency (NIMET), Abuja, Nigeria, Available at [access date : 30.11.2017]: <http://nimet.gov.ng/sites/default/files/publications/2012-seasonal-rainfall-prediction.pdf>.

Ofoegbu, C.J., Akubugwo, E.I., Dike, C.C., Maduka, H.C.C., Ugwu, C.E., Obasi, N.A., 2013. Effects of heavy metals on soil enzymatic activities in the Ishiagu mining area of Ebonyi State-Nigeria. *IOSR Journal of Environmental Science, Toxicology and Food Science* 5(6): 66-71.

Ogunkunle, C.O., Fatoba, P.O., 2014. Contamination and spatial distribution of heavy metals in topsoil surrounding a mega cement factory. *Atmospheric Pollution Research* 5(2): 270–282. Doi: <https://doi.org/10.5094/APR.2014.033> .

Oludoye, O. O. and Ogunyebi, L. A., 2017. Nutrients Assessment of Tropical Soils Around A MegaCement Factory In Southwest Nigeria. *Journal of Ecological Engineering*. 18(2): 18-25.

Poli, A., Salerno, A., Laezza, G., di Donato, P. and Dumontet, S., 2009. Heavy metal resistance of some thermophiles: potential use of alpha-amylase from *Anoxybacillusamylolyticus* as a microbial enzymatic bioassay. *Research in Microbiology*. 160: 99-106.

Ramamoorthy, D., 2015. Assessment of heavy metal pollution and its impacts on soil physical, chemical properties and β -glucosidase activities in agricultural lands, Puducherry region. Project Report. Department of Science, Technology and Environment Government of Puducherry. 45pp

Sato, J.H., de Figueiredo, C.C., Marchão, R.L., Madari, B.E., Benedito, L.E.C., Busato, J.G., de Souza, D.M. 2014. Methods of soil organic carbon determination in Brazilian savannah soils. *Scientia Agricola* 71(4): 302-308. Doi: <http://dx.doi.org/10.1590/0103-9016-2013-0306> .

Utoho, E.B., Tewari, L., 2014. Soil enzymes as bioindicators of soil ecosystem status. *Applied Ecology and Environmental Research* 13(1): 147-169. Doi: https://doi.org/10.15666/aeer/1301_147169 .

Wainwright, M., Duddridge, J. E., Killham, K., 1981. Assay of α -amylase in soil and river sediments: its use to determine the effects of heavy metals on starch degradation. *Enzyme and Microbial Technology* 4: 32-34.

Wang, Y.P., Shi, J.Y., Wang, H., Lin, Q., Chen, X.C., Chen, Y.X., 2007. The influence of soil heavy metals pollution on soil microbial biomass, enzyme activity, and community composition near a copper smelter. *Ecotoxicology and Environmental Safety* 67(1): 75–81. Doi: <https://doi.org/10.1016/j.ecoenv.2006.03.007>.

Wright, A.L., Reddy, K.R., 2001. Heterotrophic microbial activity in northern Everglades wetland soils. *Soil Science Society of America Journal* 65(6): 1856–1864. Doi: <https://doi.org/10.2136/sssaj2001.1856>.

Yun, S. and Yu, C., 2015. Immobilization of Cd, Zn, and Pb from Soil Treated by Limestone with Variation of pH Using a Column Test. *Journal of Chemistry*. <http://dx.doi.org/10.1155/2015/641415>.

Zhang, X., Li, F., Liu, T., Xu, C., Duan, D., Peng, C., Zhu, S., Shi, J., 2013. The variations in the soil enzyme activity, protein expression, microbial biomass, and community structure of soil contaminated by heavy metals. *ISRN Soil Science* Article ID 803150. Doi: <http://dx.doi.org/10.1155/2013/803150>.



Opportunities for growing lavender in areas facing natural constraints exemplified by the Borika village, Bulgaria. Zorintsa Mitreva, Veselin Pankov



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Abstract:

Areas facing natural constraints represent a serious obstacle for Bulgarian farmers and to a great extent limit their development. In this regard, it is necessary to look for alternative options for optimal use of these areas so that they are as efficient as possible despite the limitations they have.

The paper presents the basic requirements of lavender in terms of climatic and soil conditions. There is also a soil and climate characterization of a village located in area of high altitude - the land of the village of Borika, Sofia in order to be able to indicate which soil types in the Borika land are best suited for lavender growing.

Key words: field ratings, soil, soil characteristics, lavender

Introduction

The land of the village of Borika is located in the Southwest region of Bulgaria, Ihtiman municipality, Sofia district. It falls in a mountainous area with an altitude of 700 - 990 m. The total area of Borika is 294,75 ha.

The soil resources in the area were studied in the large-scale soil mapping with scale 1:10 000, conducted by scientists of Nikola Pushkarov Institute of soil science, agrotechnologies and plant protection. In the land of the village there are 11 soil types, for each are presented detailed soil characteristics, which are related to the cultivation of lavender: soil texture (contains soil texture of the plowed horizon with $< 0,01$ mm particle size in %, the soil texture of the soil under the plowed horizon $< 0,01$ mm particle size in % (Kachinskiy, 1958), humus horizon depth (cm), soil profile depth (cm), soil reaction in H_2O (pH in water extraction – measured potentiometrically (WTW 720 pH meter)), texture coefficient (which is the % clay content in the B horizon divided by the % clay content in the A horizon with particles < 0.001 mm (Kachinskiy, 1958), humus content was estimated by the Turin method (Donov et al., 1974).

According to the European Union Regulation currently (2018) in force (Regulation (EU) No 1305/2013) Annex III the biophysical criteria for the delimitation of areas facing natural constraints Borika village falls into an area facing natural constraints.

Borika village is a mountainous region that has soil types with unfavorable texture (low content of particles $< 0,01$ mm) and stoniness, shallow rooting depth (depth ≤ 30 cm) and poor chemical properties (acidity ≤ 5).

Lavender

Lavender (*Lavandula vera* L), belongs to the *Lamiaceae* family, which is major oil crop for the temperate climate zone and for Bulgaria. The Mediterranean countries, France, Spain, Italy and the Balkans are where the lavender originated (Reed, 2000). Lavender is a good honey-bearing and soil-strengthening plant. It is a perennial shrub, evergreen tuft.

Lavendula angustifolia grows 60-80 cm and has fragrant violet flower spikes of 3-7 cm (Reed, 2000). Spike lavender or *L. latifolia* (syn. *L. spica*) is also native to the western Mediterranean region and Portugal. It is later flowering and shorter than *Lavendula angustifolia* and the oil has a distinct camphoraceous odor (Reed, 2000). Important species are *Lavendula dentata* and *Lavendula stoechas* (Ernst, 2017). The root reaches a depth of 2-3 m (Koedzhikov et. al., 1971). It requires warm weather, strong solar radiation and lack of strong air currents. These requirements are largely satisfied on southern mountain slopes, protected from winds and over 800-1000 m height above the sea level (Koedzhikov et. al., 1971). During flowering changing and cloudy weather, as well as frequent precipitation, have the effect of lowering essential oil yields and deteriorating quality (Koedzhikov et. al., 1971).

Lavender tolerates low temperatures at an early stage of development of -8°C , -10°C (Koedzhikov et. al., 1971). Adult plants with sufficient snow cover can withstand up to -25°C , -30°C (Koedzhikov et. al., 1971). High summer temperatures adversely affect oil quality (Reed, 2000).

Lavender is very demanding in terms of light. When there is strong shading the oil in the flower decreases by 50% (Koedzhikov et. al., 1971). Requirement for moisture is not so demanding, it is drought-resistant, and excessive moisture gives negative results (Koedzhikov et. al., 1971). High summer temperatures adversely affect oil quality (Reid, 2000).

The crop is not demanding with respect to soils. It develops optimally on loose, air-permeable, easily absorbing heat and rich in humus and lime soils (Koedzhikov et. al., 1971). Of particular importance to the high productivity of lavender is the soil reaction. Soils of neutral (7) pH are preferred but successful crops have been produced over the range 5.8 to 8.3 pH (Reed, 2000). Lavender is best established on sandy loamy soils (Ernst, 2017). The crop is most successful when grown on well-drained soils (Ernst, 2017). Inappropriate are heavy, waterlogged and acidic soils with a high level of groundwater, as well as soils with high clay content (Koedzhikov et. al., 1971).

The main objectives of the study are:

- (1) *Present soil and climatic characterization of the land.*
- (2) *Consider the lavender requirements for the main soil climatic characteristics to indicate which soil types in the land are suited for cultivation and which are impossible for cultivation.*

Materials and Methods

The data, interpreted below are from the Vakarrel and Sofia meteorological stations, published (officially) by NIMH-BAS and summarized for a minimum of 45 years (Climate reference book for Bulgaria, 1978, 1983, 1990). Of particular importance in agriculture is the duration of the period with average daily air temperatures above a certain limit and the temperature sums for it. "Methods for working on the agricultural land cadastre in the Republic of Bulgaria" (Petrov et al., 1988) uses these characteristics with a lower limit of 10°C . The temperature sums for this period are called "active temperature sums" and are defined by Equation 1:

$$\Sigma T^{\circ}\text{C} > 10^{\circ}\text{C} = (t_1 + t_2 + t_3 + \dots + t_n) \quad (1)$$

Where:

$\Sigma T^{\circ}\text{C} > 10^{\circ}\text{C}$ - the sum of effective temperatures (for the period with average daily temperature $> 10^{\circ}\text{C}$) in $^{\circ}\text{C}$;

$t_1, t_2, t_3, \dots, t_n$ - consecutive observations of mean 24-hour temperatures of air in $^{\circ}\text{C}$;

1, 2, ... n - index for serial number of the day through the period of measurement.

The land capability approach uses the so-called limitation method, which implies comparing land characteristics of a land unit with critical limits of each capability class. The values of land characteristics are tested first against the limits of the highest capability class and, unless all the limits are met, the land unit automatically falls to the next lower class (Van Lanen, 1991). This sieving process continues until a capability class is found at which all the limits are met. This means that if one limitation is of sufficient severity to lower the land unit to a lower class, it is allocated to that class, no matter how favorable the other land characteristics may be (law of minimum) (Van Lanen, 1991). The results are harmonized with classes from the FAO framework (FAO, 1976, 2007).

The nature of the severest limitation, e.g. erosion, excess water or climatic limitation, is specified in the capability assessment (Van Lanen, 1991). Refinements are possible by making the suitability class ratings dependent on more than one limiting land characteristic (Rosa, Diepen, 2002).

Simple limitation method compares the plant requirements with its corresponding qualitative land and climatic characteristics and the most limiting characteristics defines land suitability class (Darvishi-Foshtomi et al., 2011).

The limitation method concerns the selection of the most restricting criterion rate and considering it as the total score for a land unit (Sharififar, 2012). This method defines land classes with regard to number and intensity of limitations (Chadar et al., 2018, Sys et al., 1991).

Results and Discussion

Climatic characteristic

The land of the village of Borika falls into the Moderate Continental Climatic Sub-Area and more precisely in the climatic region of the high fields of Western Central Bulgaria. The climatic region of the highlands of Western Central Bulgaria consists of separate valleys located in the western part of Central Bulgaria and surrounded by many low and medium altitude mountains. Winter in the region is cold, but the summer is cooler. Typical of the area are late spring and early autumn frosts, due to the valley nature of the terrain.

Precipitation

Table 1. Average monthly and average annual precipitation. (Vakarel meteorological station)

Month	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Annual sum
mm/m ²	42	37	44	55	85	82	63	44	40	49	49	47	635

Table 1. shows that the maximum rainfall is in June and the minimum is in February in the nearest Vakarel meteorological station. The average annual precipitation is 635 mm / m² (Climate reference book for Bulgaria, 1990).

The mountainous region of Borika has sufficient precipitation for lavender as the crop is not very demanding in terms of water needs.

Temperature characteristics

As a start date of sustained air temperature above 10⁰C for the area is indicated 29 April and for the final is 9 October (Climate reference book for Bulgaria, 1983, p.173). The duration of days with sustained air temperature > 10⁰C for the area is 162 days and the temperature sum is 2510⁰C for this period. (Climate reference book for Bulgaria, 1983 (p.

179)) as is indicated by the nearest Vakarel meteorological station. This implies good conditions for the development of lavender during vegetation.

Characteristics of solar radiation

One of the most important condition for lavender growing is the amount of solar radiation, the hourly and daily sums of direct photosynthetic active radiation in a cloudless sky on the horizontal surface are presented.

Photosynthetic active radiation (PAR) is that part of the solar radiation with a wavelength of 0,38 to 0,71 μm , which is used during photosynthesis. The nearest meteorological station for which there is data is used and data are presented in Table 2. Due to low variation because of low distances in latitude and longitude the territory of Bulgaria does not experience big changes in the solar radiation (Climate reference book for Bulgaria, 1978). The total sum of PAR is sufficient for the vegetation cycle as it is the most important factor for growing lavender that has a direct effect on the quality of the yield.

Table 2. Hourly and daily sum of total photosynthetic active radiation (PAR) in cloudless sky (cal./cm^2). Sofia meteorological station

Month	Sunrise 5.30	5. ³⁰ - 6. ³⁰	6. ³⁰ - 7. ³⁰	7. ³⁰ - 8. ³⁰	8. ³⁰ - 9. ³⁰	9. ³⁰ - 10. ³⁰	10. ³⁰ - 11. ³⁰	11. ³⁰ - 12. ³⁰	12. ³⁰ - 13. ³⁰	13. ³⁰ - 14. ³⁰	14. ³⁰ - 15. ³⁰	15. ³⁰ - 16. ³⁰	16. ³⁰ - 17. ³⁰	17. ³⁰ - 18. ³⁰	18. ³⁰ - 19. ³⁰	Daily sum
I				2,6	6,4	10,1	13,4	14,8	14,0	11,5	7,3	2,0				82,1
II			0,6	5,7	10,8	16,6	20,6	23,0	22,1	18,6	13,3	7,8	1,5			140,6
III		0,3	4,6	10,5	17,0	22,1	26,2	27,5	27,0	24,8	20,1	12,8	5,9	0,6		199,4
IV		0,2	2,8	11,0	18,0	23,7	28,5	31,2	32,1	31,6	28,8	23,0	17,6	9,2	1,8	259,5
V	1,2	6,1	13,0	20,0	26,5	31,3	35,0	36,6	35,9	32,2	26,5	18,8	12,7	6,1	0,7	302,6
VI	2,0	7,5	14,4	21,3	27,5	31,7	34,7	37,2	37,7	33,5	22,4	21,5	15,3	8,0	1,8	316,5
VII	1,2	7,6	14,6	20,4	26,4	31,0	35,2	37,0	36,0	32,7	28,1	21,5	14,3	7,3	1,4	314,7
VIII	0,2	2,4	5,9	11,9	18,2	23,5	28,9	32,3	33,5	32,5	29,1	23,9	17,1	9,1	0,4	268,9
IX		1,2	4,5	9,1	15,4	21,1	25,8	28,6	29,1	27,9	23,8	17,7	10,0	0,6		214,8
X		0,2	2,1	5,6	10,9	16,4	20,4	23,2	23,7	22,0	17,1	10,5	4,6			156,7
XI			0,6	2,7	9,4	14,3	16,8	17,8	15,9	11,9	7,3	1,6				98,3
XII				1,4	6,5	10,5	13,2	14,5	12,9	9,5	4,8	0,6				73,9

Soil characteristics

On the territory of the village of Borika there are 11 soil types classified according to WRBSR 2014 update 2015 (IUSS Working Group WRB, 2015), with soil texture predominating from low to medium sandy clay according to Bulgarian soil texture classification (№ 1,2,3,4,6), followed by № 5,7,9 and low sandy-clayey № 8 and 10, as well as sandy №11. The humus horizon's depth varies depending on the soil type (10-30 cm) and all the soils are with low depth. According to the depth of the profile the soils with low depth (№ 7,8,9,10,11) and moderate depth (№4,5,6) predominate, followed by deep (№2,3) and highly deep (№1). The soils in the region have a low texture differentiation (Texture coefficient) ranging from 0.9 to 1.5, with the exception of №3 and №5, which are highly differentiated. The soil response ranges from moderately acidic to slightly acidic (pH in H_2O 4,8- 6,0). According to the humus content the soils are low to medium humus (1-3,1%), the

groundwater level is deep, over 600 cm. Affected by erosion are almost all soil types with the exception of (№1, №2, №3).

Table 3. Matrix of soil characteristics

№	Soil type WRBSR 2014, u 2015.	<0,01 in plowed horizon (%)	<0,01 in area under plowed horizon (%)	Humus horizon depth (cm)	Soil profile depth (cm)	Texture coefficie nt	pH in H ₂ O	Hu mus (%)	Suitabil ity
1	Fluvisols	35	38	30	160	1.3	6	2.1	A
2	Phaeozems	34	39	30	150	1.3	5.3	1.2	A
3	Planosols	37	60	25	100	2.2	5.5	1.4	A
4	Luvisols	39	49	25	95	1.5	5.3	2.4	A
5	Planosols	14	51	10	70	4.7	4.8	1.2	B
6	Cambisols	40	26	20	65	1.1	5.6	1.3	A
7	Leptosols	14	14	15	20	1	5.3	1	B
8	Cambisols	28	20	20	40	1.3	5.4	1.4	B
9	Leptosols	16	12	20	40	0.9	5.1	1.7	B
10	Leptosols	25	25	15	15	1	5	3.1	B
11	Leptosols	8	8	10	20	1	5.3	1	B

Farmers need efficient practical recommendation for decision making and risk avoiding. A variant of the limitation method is proposed where a matrix of characteristics is created. This is a mountainous region with lands facing natural constraints and there are limitations for agriculture. With –A” are represented the soils that can be used for growing lavender with a lower risk, corresponding to the FAO S order(S1, S2, S3) and with –B” are represented the soils that have limiting factors of significance that make them non-suitable for growing lavender, corresponding to FAO N order (N1, N2) for Borika village (FAO, 1976, 2007).

Table 4. Matrix of land characteristics evaluation

№	<0,01 in plowed horizon (%) >30	<0,01 in area under plowed horizon (%) >30	Humus horizon depth (cm) >15	Soil profile depth (cm) >50	Texture coefficient <0,9 <1,5	pH in H ₂ O >5.2	Humus (%) >1	Count Y
1	Y	Y	Y	Y	Y	Y	Y	7n
2	Y	Y	Y	Y	Y	Y	Y	7n
3	Y	Y	Y	Y	N	Y	Y	6t
4	Y	Y	Y	Y	N	Y	Y	6t
5	N	Y	N	Y	N	N	Y	3ca,ha,t,p
6	Y	N	Y	Y	Y	Y	Y	6cb
7	N	N	N	N	Y	Y	N	2ca,cb,ha,d,hb
8	N	N	Y	N	Y	Y	Y	4ca,cb,d
9	N	N	Y	N	N	N	Y	2ca,cb,d,t,p
10	N	N	N	N	Y	N	Y	2ca,cb,ha,d,p
11	N	N	N	N	Y	Y	N	2ca,cb,ha,d,hb

The small letter represents the soil limitation factors according to the legend:

n – no limitations;

ca – clay content in plowed horizon limitations (%);

cb - clay content under plowed horizon (%);

ha – humus horizon depth limitations;

d – soil profile depth limitations;

t – texture coefficient limitations;
 p – pH limitations;
 hb – humus content limitations.

With —Y” are represented the soils that fall under criteria for growing lavender and with —N that do not.

As it is seen, the best soils in the region for growing lavender are 1, 2, 3, 4, and 6. As lavender tuft is not growing very deep it can tolerate slight differences in texture coefficient. The clay content in number 6 is closer to the limit and it has points close to the maximum sum of 7 (26). They all have equal to or more than 5 —Y”s. Number 5 is very acidic, with very shallow humus horizon and unfavorable soil texture, number 7, 8, 9, 10 and 11 are with very low depth and/or unfavorable soil texture and/or humus content and/or acidity.

For greater visibility in Fig. 1 and Fig. 2 maps of the studied area are also presented. The large-scale (1:10000) map of the land (digital archive of ISSAP "N. Pushkarov", digitized by EASR, MAF) includes 11 soil mapping units and is shown in Fig. 1. Note that these are images not actual maps with scale. Not all of the land is used for agriculture. Some of the land is covered with water, forests, roads, buildings.

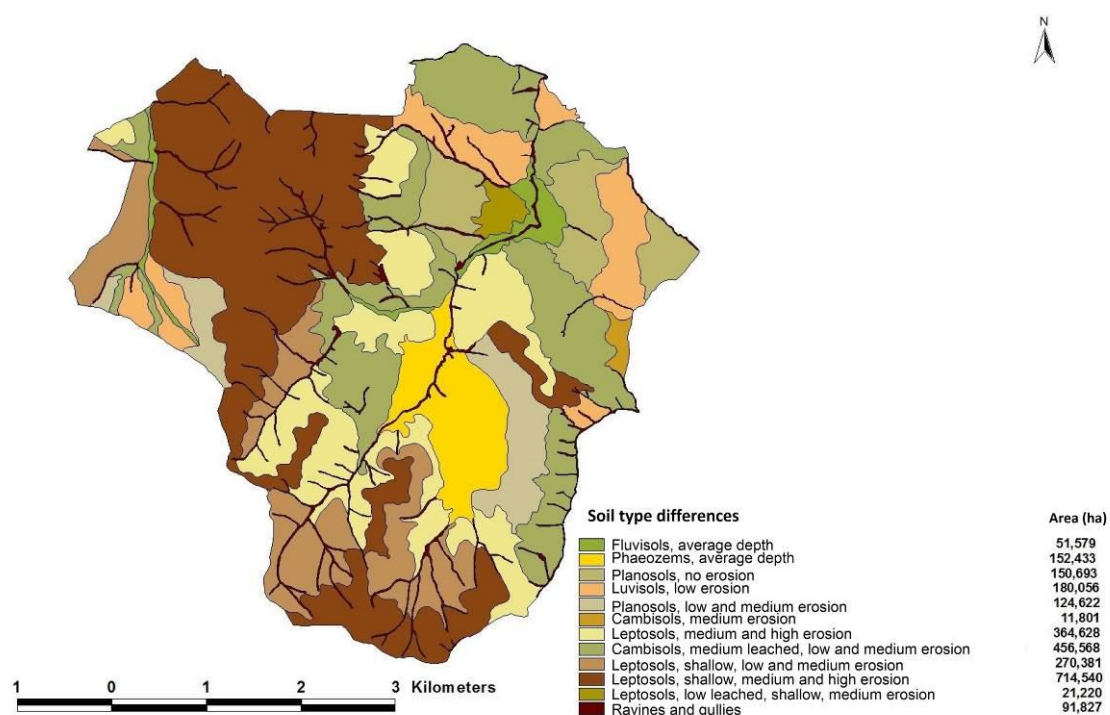


Figure 1. Soil map of Borika village, Ihtiman district, Scale 1:10000

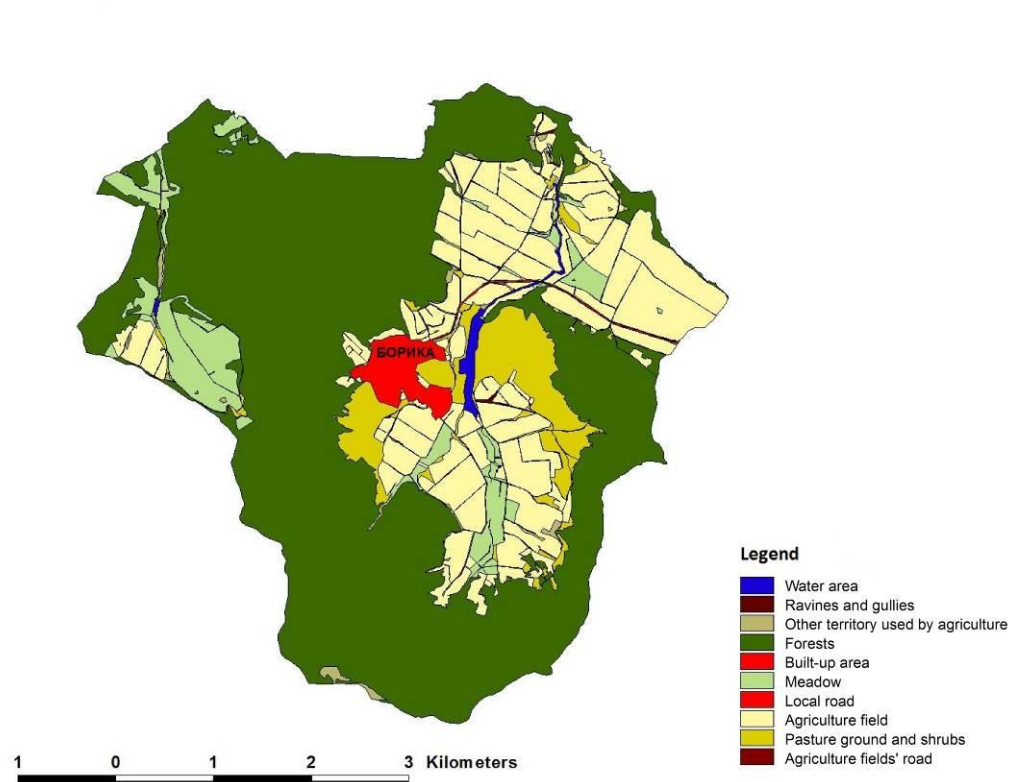


Figure 2. Map of distribution of the land of Borika village according to methods of long-term use

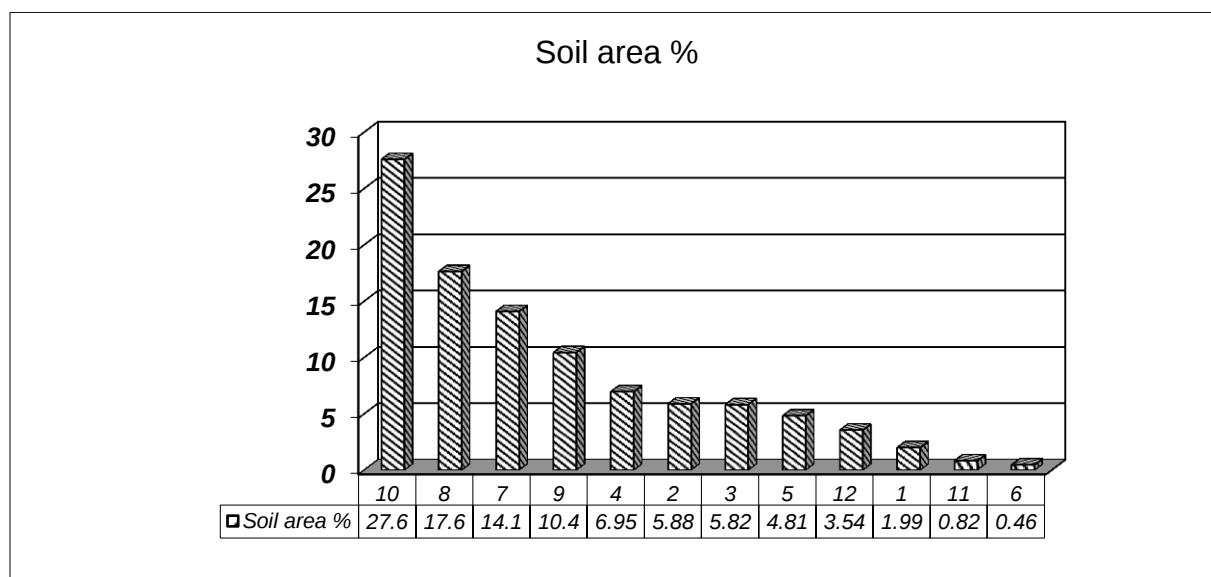


Figure 3. Area of soil units by number

Conclusion

It is more difficult to grow lavender in areas facing natural constraints. One of the units in the legend are not soils. These are ravines and gullies according to the Bulgarian soil map. Most of the area is covered with soil number 10, 8 and 7 (Figure 3).

The best soils for growing lavender are with number 1,2,3,4, 6 (representing Fluvisols, Phaeozems, Planosols, Luvisols and Cambisols) and they cover only 21,1% of the land. They are located near the rivers and in specific valleys with small slopes and are most suitable for growing lavender. In conditions that face natural constraints growing lavender should be cautious.

References

- Chadar, B. R., Vaidya, P. H., Kachave, R. R., & Aundhakar, A. V., 2018. Characterizations, classifications and soil site suitability evaluation of soils of farm College of Agriculture, Latur, Maharashtra.
- Climate reference book for Bulgaria v. 1., 1978. Solar radiation and solar heat. GUKHM, BAN, Izd. "Nauka i izkustvo", Sofia. (in Bulgarian).
- Climate reference book for Bulgaria v. 3., 1983. Air temperature, soil temperature, frost. GUKHM, BAN, Izd. "Nauka i izkustvo", Sofia. (in Bulgarian).
- Climate reference book for Bulgaria, 1990. Precipitation in Bulgaria. GUKHM, BAN, Izdatelstvo na Bulgarska academia na naukite, Sofia. (in Bulgarian).
- Darvishi-Foshtomi, M., Norouzi, M., Rezaei, M., Akef, M., & Akbarzadeh, A., 2011. Qualitative and economic land suitability evaluation for tea *Camellia sinensis* L. in sloping area of Guilan, Iran. *J. Biol. Environ. Sci.*, 515, 135-146.
- D. de la Rosa and C.A. van Diepen. 2002. Qualitative and Quantitative Land Evaluation, in 1.5. Land Use and Land Cover, in *Encyclopedia of Life Support System (EOLSS-UNESCO)*, Eolss Publishers. Oxford, UK. [<http://www.eolss.net>].
- Donov, V., S. Gencheva, K. Yorova. 1974. A manual for practical seminars in Forest soil science. Zemizdat. Sofia. p. 216. (in Bulgarian).
- Ernst, M., 2017. *Lavender*. CCD-CP-127. Lexington, KY: Center for Crop Diversification, University of Kentucky College of Agriculture, Food and Environment. Available: www.uky.edu/ccd/production/crop-resources/nursery-ornamental/lavender.
- FAO., 1976. A framework for land evaluation. *FAO Soils Bull.* No: 32. FAO, Rome. pp: 71.
- FAO., 2007. Land evaluation towards a revised framework. *Land & Water Discussion Paper 6*. FAO, Rome, p. 124.
- IUSS Working Group WRB., 2015. World Reference Base for Soil Resources 2014, update 2015 International soil classification system for naming soils and creating legends for soil maps. *World Soil Resources Reports No. 106*. FAO, Rome.
- Kachinskiy N.A., 1958. Mechanical and microaggregate texture of soil, methods of its study. Moscow. Pub. A.S. USSR. — S. 25. — 191 p. (in Russian).
- Koedzhikov, Hr., G. Koinov, M. Lazarov, M. Maslinkov, 1971. Plant growing. Zemizdat. Sofia. (in Bulgarian).
- Petrov, E., Iv. Kabakchiev, P. Bozhinova, A. Stoeva, Y. Georgieva, E. Hershkovich, D. Dilkov, 1988. Methods for work on the agricultural land cadastre in Bulgaria. NAPS Association. (in Bulgarian).
- Regulation EU No 1305/2013 of the European Parliament and of the Council of 17 December 2013. on support for rural development by the European Agricultural Fund for Rural Development EAFRD and repealing Council Regulation EC No 1698/2005 OJ L 347, 20.12.2013, p. 487–548 BG, ES, CS, DA, DE, ET, EL, EN, FR, GA, HR, IT, LV, LT, HU, MT, NL, PL, PT, RO, SK, SL, FI, SV.

Reid, A., 2000. Growing lavender in Western Australia. Department of Agriculture and Food, Western Australia, Perth. Bulletin 4454.

Sharififar, Amin, 2012. Assessment of different methods of soil suitability classification for wheat cultivation. Journal of Agrobiology. 29. 10.2478/v10146-012-0008-0.

Sys C, Van Ranst E, Debaveye J., 1991. Land Evaluation Part I, II. Red-edited valums of publication no. 7 of the general Administration of Cooperation Development, Brussels, Belgium, 274.

Van Lanen, H.A.J., 1991. Qualitative and quantitative physical land evaluation: an operational approach. Doctoral thesis. Agricultural University Wageningen, the Netherlands, xiv + 196 pp.. 59 Figures and 16 Tables.



Changes in Biomass Accumulation and Soil Properties After Fertilization of Ryegrass.

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Abstract

A containers experiment was carried out in four variants with fertilization of ryegrass: 1st and 2nd trials, with the addition of 1ml and 5ml of organic fertilizer "Siapton" and 3th and 4th trials: a combination of Siapton (0.5 ml fertilizer in 50 ml of water) with the mineral fertilizer "Kristalon" in quantity of 0.5 and 2 grams respectively. There was used also a control. It is accounted a higher accumulation of organic matter (content of C% and N%) in leaves of ryegrass after fertilizing in comparison with the control. Accumulation of dry matter also is higher in fertilized variants ($27.09 \div 37.62$) compared to the control (25.99g). This difference is not confirmed and does not recorded in relation to the roots of ryegrass. Acidification of soils is changed towards a higher pH ($5.5 \div 6.4$) in fertilized variants in comparison with the control (pH = 5.2). The humus composition was studied by the method of Kononova - Belchikova, but apparent differences were not accounted in relation to the use of organic and mineral fertilizers. The content of humic acids extracted with pyrophosphate calculated according the weight of soil samples is lowest in control (1.02%), where the content of fulvic acids is high (0.40%).

Key words: organic mass, dry weight, humic and fulvic acids

Introduction

Ryegrass (*Lolium Perennel L.*) is a short-lived grassy species. It is used as a forerunner of many crops as it develops a powerful root system and thus improves the soil structure, increases overall soil moisture and nitrifying ability. Ryegrass has a special place in the cities, the landscaping of recreational areas and sports grounds. It also participates in improving the aesthetic features of gardens, parks, family houses and amusement facilities. As a one-year-old grassy species, ryegrass also has a place into the composition of many fodder mixtures. Rich in protein and energy quality high-quality fodder is obtained by cross-sowing of ryegrass and white clover (Mihovski and Sabeva, 2011). As a forage culture, it can also be used in a number of agroforestry systems (Kachova et al., 2018). And this: increasing the yield and quality of forage and creating weed-free areas is an important part of the tasks in modern agriculture. Ryegrass is also used for afforestation of lead-contaminated lands to cover the objectives of phytoremediation (Bgantzova, 2009). Petrova (1992) uses the fertilization of ryegrass during its cultivation on heavy metals contaminated substrates of phosphogypsum and pyrite sludge in order to improve its state. Ryegrass reacted violently after the fertilizers were brought into. Fertilization has a positive effect on its state. In general, it can be affirmed

that the use of fertilizers in ryegrass cultivation leads to an increase in yield, improvement of its condition and reduction of negative effects (Vassilev, 2004, 2006, Dimitrova, 1995). Fertilization can also improve soil properties (Valchovski et al., 2014).

The aim of the present study is to trace the effect of fertilization of ryegrass with organic and mineral fertilizers on the accumulation of biomass and the soil properties.

For this purpose organic fertilizer are used - "Siapton", which is new for the Bulgarian market and mineral fertilizer "Kristalon", rich in N, P, K and other nutrients.

Material and Methods

In the spring of 2017, ryegrass (*Lolium Perennel* L.) was seeded in containers of 500ml volume in a dose of 0.2 grams seeds per container. The soil was sieved and cleaned up by roots. Soil type is *Vertisols* and it was taken from the yard of the Forest Research Institute - BAS. After 29 days fertilizers were applied and after 30 days treatment was repeated. The following experimental variants were used:

- Treatment1. Fertilizing with 1 ml of "Siapton" organic fertilizer dissolved in 50 ml of water.
- Treatment 2. Fertilizing with 5 ml of "Siapton" organic fertilizer dissolved in 50 ml of water.
- Treatment 3. Fertilizing with 0.5ml organic fertilizer "Siapton", dissolved in 50ml of water and 0.5g „Kristalone” mineral fertilizer.
- Treatment-4. Fertilizing with 0.5ml organic fertilizer "Siapton", dissolved in 50ml of water and 2g “Kristalone” mineral fertilizer.
- Treatment 5 - control without fertilizing.

Each treatment was repeated in 7 repetitions. The control was in 14 repetitions. Thus, all containers with the control were 49 in numbers.

Throughout the experiment, constant moisture was maintained, with even watering of all containers. The organic fertilizer "Siapton" was developed on the basis of naturally hydrated proteins from firm "Chemtura Europe Limited", UK. This organic fertilizer is specialized in increasing yield and quality of production and activating protection forces of crops. The composition given by the manufacturer is: total organic ammonium nitrogen up to 4%; organic carbon - 25%; amino acids with animal origin - 54.34%. The “Kristalon” mineral fertilizer is a production of firm "Hydro Agro Rotterdam", the Netherlands. Contains N, P, K, Mg as the main ingredient and other trace elements.

In September, the ryegrass was removed with the roots, washed and dried at 105 ° C to a constant dry weight. Plant samples (roots and leaves) for C and N content were taken. Carbon was determined with a bichromic mixture (0.4N K₂Cr₂O₇ + k.H₂SO₄) in a plant sample of 0.05g through the method for determination of carbon in soil samples (Donov et al., 1974). The nitrogen in the plant samples was burnt with k.H₂SO₄ and H₂O₂ and determined with a Parnas-Wagner apparatus with 50% NaOH and titrated with 0.02N H₂SO₄. Soil samples were analyzed for C - Thurin method, N - Keldahl method, and composition of humus - by the method of Kononova - Belchikova (1961).

Results and Discussion

After dry weight measurement, it has been found that fertilization produces a corresponding effect in the accumulation of biomass in the grassland. The results are presented in Fig. 1. On the figure are also given the weight of the roots.

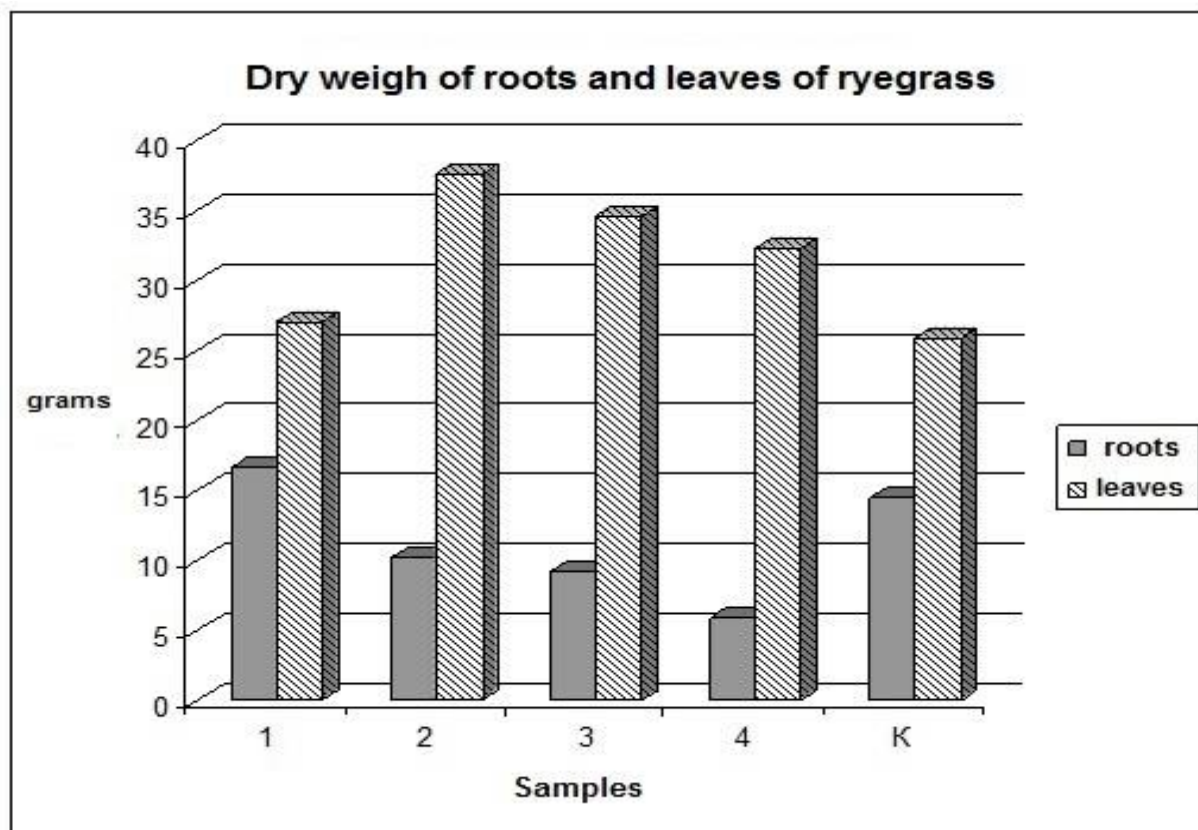


Figure 1. Dry weigh of roots and leaves of ryegrass

The biomass of the roots far exceeds that which is accumulated in the leaves. It confirms the fact that ryegrass develops a powerful root system. The lowest is the weight in the unfertilized variant - the control. The best is accumulated leaf biomass in the ryegrass of Treatment 2, in which we used the largest amount of organic fertilizer "Siapton" - 5 ml, dissolved in 50 ml of water. In the roots, this effect is not observed. Fertilization, including with mineral fertilizer, does not affect the accumulation of biomass in the roots. On the contrary, the untreated variant (the control) also accumulates a large amount of root mass.

Particularly well fertilization influences the content of carbon and nitrogen in the leaves - fig. 2, especially that of carbon.

The control has the lowest amount of carbon stored in the leaf mass of ryegrass. Fertilizing with "Siapton" organic fertilizer improves the carbon and nitrogen accumulation in the leaves, especially when using more fertilizer - Treatment 2 (5ml). Especially advantageous is the use of "Kristalon" mineral fertilizer (Treatment 3 and Treatment 4). The maximum amount of carbon and nitrogen we have at the experiment with the lower dose of "Kristalon" (Treatment 3). Perhaps the higher dose is not well combined with the use of the organic fertilizer "Siapton".

This is not the case with the accumulation of carbon and nitrogen in the roots of ryegrass - fig. 3. Even on the contrary, the control also has significant carbon and nitrogen content in the roots. Here we found a lack of effect from fertilization with here used specific fertilizers with specific doses on biomass accumulation and carbon and nitrogen content in the ryegrass roots.

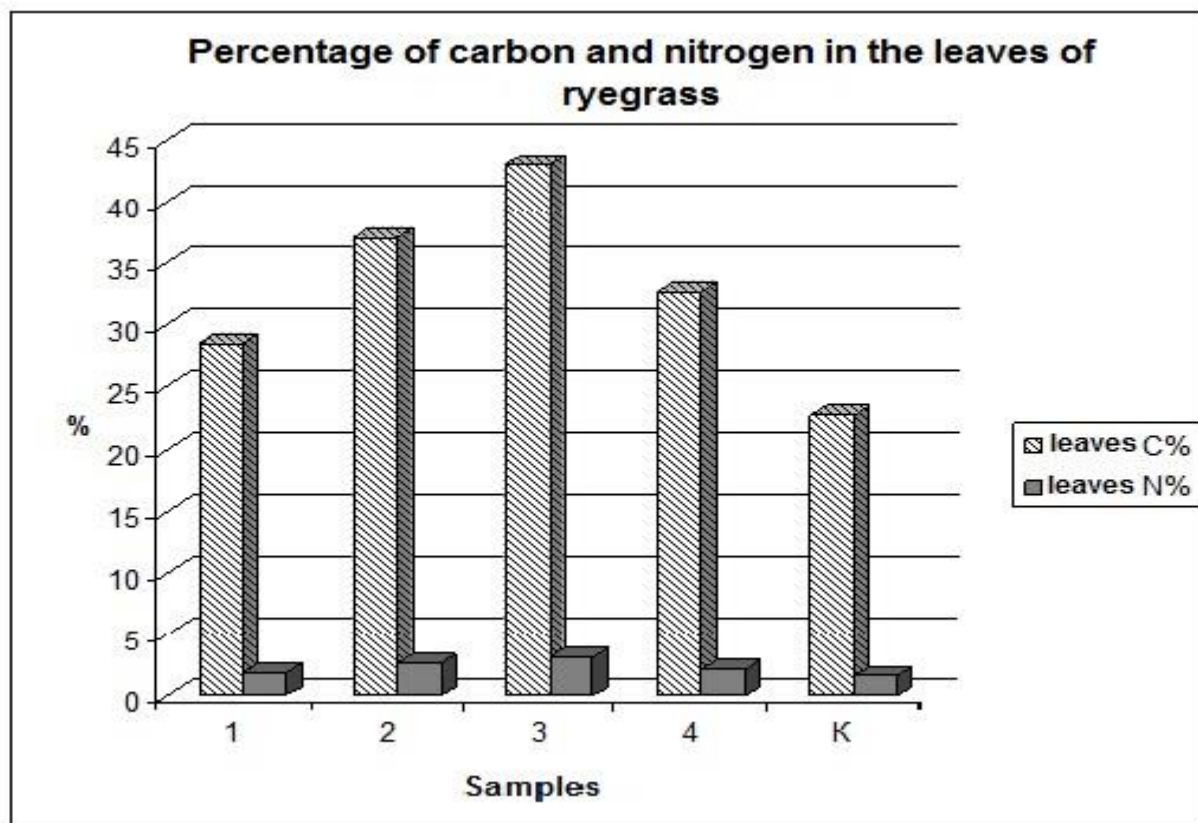


Figure 2. Percentage of carbon and nitrogen in the leaves of ryegrass

In soil studies the main results are given in Table 1. The results are mean values of the 7 repetitions.

Table 1. Main characteristics of soil

Experiment	pH	C%	N%	C/N
1	5.55	4.6	0.5	9.2
2	6.14	3.9	0.4	9.8
3	6.34	3.9	0.4	9.8
4	6.29	3.8	0.4	9.5
K	5.24	3.8	0.4	9.5

Soil acidity is favorably influenced by fertilization with organic and mineral fertilizers. From a moderate acidic reaction in the control (pH = 5.24), the acidity decreases to a slightly acidic (Treatments 2, 3, 4) which acidity is more favorable for vegetation development. The carbon and nitrogen content of the soil is also affected by fertilization. Particularly beneficial is their content in Treatment 1. But the t-test done did not show statistical proven differences between contents of C and N in fertilized variants in relation to the control. Overall, however,

in all Treatments, the C/N ratio is very low (<16), indicating that the mineralization processes in this soil are delayed and the humus formation proceeds at a low speed.

The analysis of humus composition according Cononova - Balchikova was also made. It determines the total content of humic and fulvic acids using a mixed solution of 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ and 0.1M NaOH (Table 2).

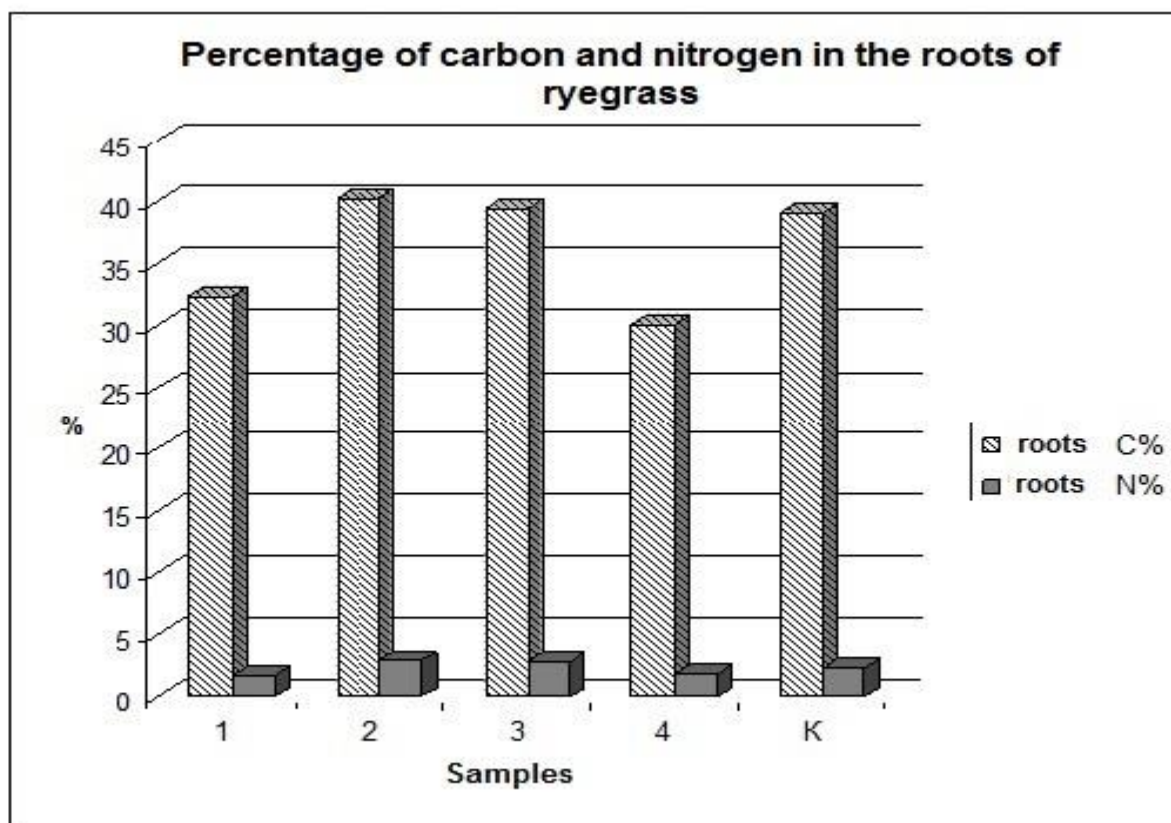


Figure 3. Percentage of carbon and nitrogen in the roots of ryegrass

The table shows the percentages of the total carbon extracted with the pyrophosphate extract; the amount of humic and fulvic acids; “aggressive” fulvic acids and carbon in the residue. Each percentage is calculated towards the weight of soil sample, taken for analysis.

Table 2. Humus composition

Experiment	C in pyrophosphate extract %	Humic acids %	Fulvic acids %	C in the residue %	“Aggressive” Fulvic acids %
1	1.59	1.32	0.27	2.99	0.20
2	1.72	1.25	0.47	1.66	0.19
3	1.62	1.08	0.54	2.27	0.08
4	1.42	1.15	0.27	2.40	0.23
K	1.42	1.02	0.4	2.4	0.08

Carbon in the pyrophosphate extract is low (~ 1%). On the contrary, the non-extracted carbon retained in the residue is in a higher percentage (~ 2%). Fertilization favorably affects the content of humic acids. Humic acids are more stable organic acids in composition to organic matter. They sequester of larger amounts of carbon in its composition. In this sense the effect of fertilisation is in relation with sequestration of carbon in the system. The lowest is the percentage of humic acids in the unfertilized variant (control). On the contrary, the percentage of the more unstable and more easily mobile fulvic acids in the soil is high in the control (0.4%). Aggressive fulvic acids, however, are not high in this non-fertilized variant, probably due to the low level of carbon extraction in the pyrophosphate extract.

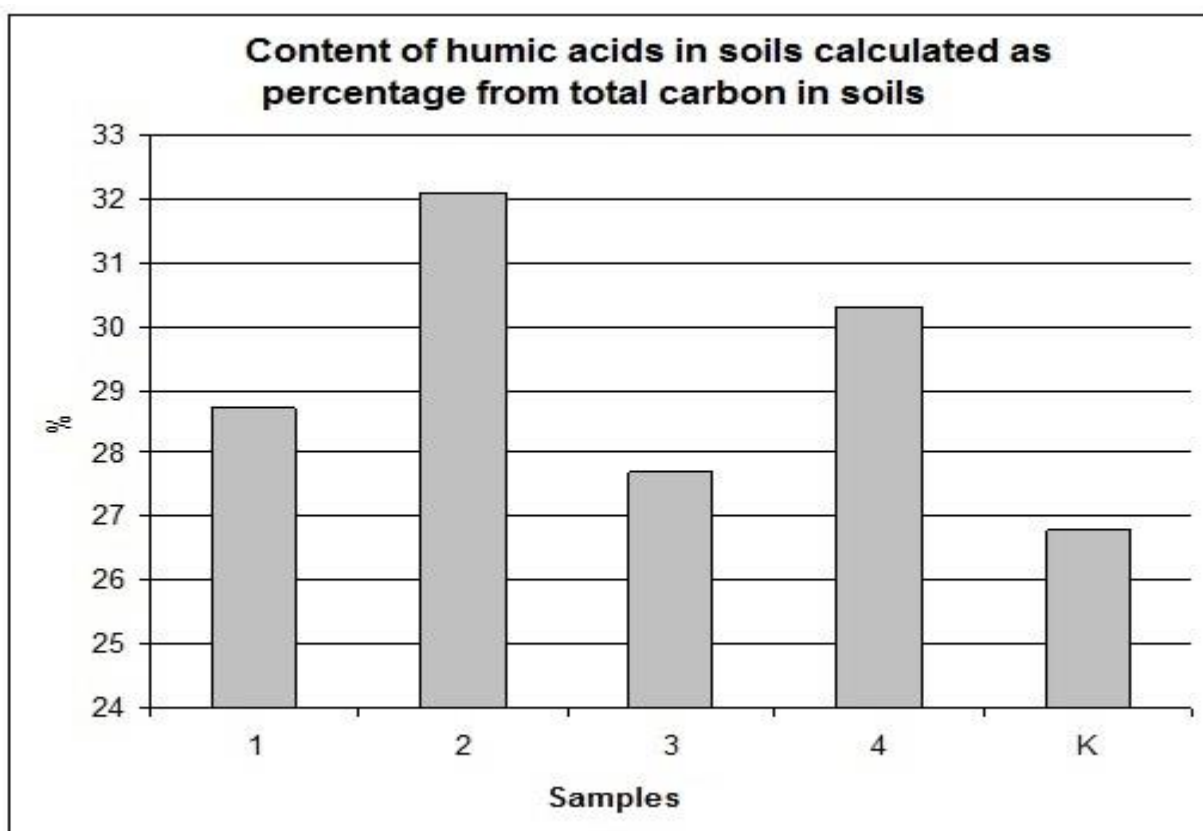


Figure 4. Content of humic acids in soils calculated as percentage from total carbon in soils

If, however, we calculate the amount of humic acids not in relation to the quantity of the sample but as a percentage of the total carbon content in the soil (Table 1), a clear picture is obtained - Fig. 4.

Clearly is highlighted the result, that the amount of humic acids is the lowest in the non-fertilized variant - the control. Hence, we can conclude that fertilization stabilizes organic matter in the soil, improving the amount of more stable forms of carbon - the humic acids. Sequestration of carbon is increased.

Conclusion

The use of organic fertilizer "Siapton" alone and in combination with "Kristalon" mineral fertilizer has a beneficial effect on the accumulation of biomass in the ryegrass, as well as on the properties of the soil. Fertilization results in:

- the accumulation of more dry matter in the leaves;
- higher carbon and nitrogen content in the foliage;
- improving soil acidity;
- better store of organic matter;
- a more favorable humus composition in the soil with a higher content of the humic acid fraction.

No repercussions of fertilization on the accumulation of biomass in the roots of ryegrass are detected. No statistical proofs were found.

References

- Bgantsova M., 2009. Use mustard sarent and ryegrass pasture for phytoremediation of lead-contaminated land. Bulletin of Tomsk State University, 324: 350-353. (in Russian).
- Dimitrova Tsv., 1995. Study on the weeds and fight against them in seed production of pasture ryegrass (*Lolium perenne* L.). Rasteniyevadni nauki, 32, 3: 168-170. (in Bulgarian).
- Donov, V., S. Gencheva, K. Yorova, 1974. Guidance on soil analyses. Sofia, Zemizdat, pp 220. (in Bulgarian).
- Kachova V., G. Hinkov, E. Popov, L. Trichkov, Rosa Mosquera-Losada, 2018. Agroforestry in Bulgaria – history, present status and prospects, Agroforestry Systems, 92, 3: 655–665.
- Kononova M., N. Belchikova, 1961. Rapid method of mineral soil humus composition. Pochvovedenie, 10: 75-85. (in Russian).
- Mihovski Tsv., M. Sabeva, 2011. New technological approaches in creation of mixt New technological approaches to the creation of mixed crops of white clover and grassland ryegrass. Journal of Mountain Agriculture on the Balkans, 14, 3: 541-547. (in Bulgarian).
- Petrova R., 1992. Results from containers experience with fertilizing grassland (*Lolium perenne* L.) grown on phosphogypsum and pyrite sludge substrates. Nauka za gorata, 2: 49-55. (in Bulgarian).
- Valchovski Y., Z. Petkova, V. Kutev, H. Pchelarova, E. Markov, A. Katsarova, 2014. Agrochemical assessment of different types of Chernozems and optimization of fertilization in basic crops. Pochvoznanie, Agrohimiya and Ecology, XVIII, 3-4: 22-30. (in Bulgarian).
- Vassilev, E., 2004. Possibilities of using spring fodder peas as a cover of seed-borne pasture ryegrass. I. Productivity of spring peas fodder grown as a shelter for pasture ryegrass for seed production. Journal of Mountain Agriculture on the Balkans, 7, 6: 536-545. (in Bulgarian).
- Vassilev, E., 2006. Possibilities of using spring fodder peas as a cover of seed-borne pasture ryegrass and its influence on the seeds yield. Field Crops Studies, III – 3: 441-446. (in Bulgarian).



International Meeting “Payment for Ecosystem Services-Forest for Water” (CA15206 PESFOR)



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A meeting related to the European scientific program COST (European Co-operation in Science & Technology) took place from 25th and 27th September, 2018 r. in the Congress Center of Flamingo Grand Hotel (Snapshot 1). Representatives of 39 countries and organizations as the European Forest Institute and the United Nations Economic Commission for Europe/ FAO participate in the cost action PESFOR-W, Snapshot 2. Chairpersons of the action are D-r Gregory Valatin (United Kingdom), and Vice Chairmen – Prof. Gebhard Shueler (Germany) [1]. The hosts of the meeting were Prof. Dr. Mariana Lyubenova from the Faculty of Biology, Sofia University and Assoc. Prof. Alexander Shikalanov from the Faculty of Information Sciences, University of Library Studies and Information Technologies, who are the members of Management Committee of the Action.



Snapshot 1. The meeting in action.

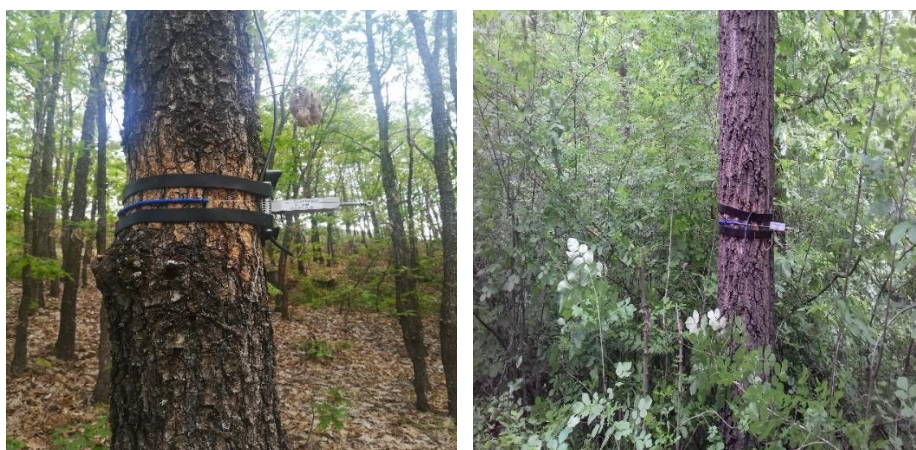


Snapshot 2. Participants in front of the Green Center.

The main objective of international scientific cooperation is to collect and validate good practices of forest ecosystem services assessment for the quantity and the quality of water in adjacent areas (selection of complex water flow and water quality indicators). The expected practical outcome of international science cooperation will be to synthesize knowledge, promote joint research to improve Europe's capacity to use Payments for Ecosystem Services (PES) for achieving the Water Frame Directive (WFD) objectives and other policy goals through incentives for planting forests to reduce diffuse pollution from agriculture. Also the result will be the development of PES Schemes, the creation of a

protocol and algorithm for calculating the cost- effectiveness of forest systems and the schemes developed.

The representatives of Bulgarian institutions presented their original achievements related to the management of water resources (Basin Directorate "Black Sea Region"), development of payment schemes (Institute for Economic Research, BAS and WWF-Bulgaria), management of forest resources in Bulgaria, mapping and assessment of forest ecosystem services and legislation developments (Executive Forest Agency, Forest Institute, BAS). The first results from the Bulgarian project „Development of an ecosystem services assessment scheme, their effectiveness for purification and protection of water and other natural components in the regions“ [2] (National Scientific Fund, Ministry of Education and Sciences), were presented (Sofia University, University of Library Sciences and Technology). Some of the first dendrometers in natural forests were tuned, installed and put into action, that monitor the 24-hour radial growth of *Quercus frainetto* Ten. and *Quercus cerris* L. Long-term observations would make it possible to create a database and participate in international projects (Snapshot 3 - 4). Professor Margaret Shannon of Baldy SUNY Buffalo Law School presented the subject "Critical Transformational Deliberative Science: A Critical Element for PESFOR - F for W".



Snapshot 3. Dendrometer on *Q. frainetto* tree. Snapshot 4. Dendrometer on *Q. cerris* tree.

One of the focus of meeting in Albena is the system of field protective forest belts in Dobrudja [3-5]. The role of wetlands for water regime of the regions, for the biodiversity protection, as a bio-carbon storage and for the natural components purification, is also on the focus of international scientific cooperation. The Bulgarian experience in the construction, maintenance and management of field protective forest belts in the Bulgarian part of Dobrudja was reported (Northeastern State Enterprise, Forest Protection Station -Varna, State Hunting Farm –Balchik, State Forestry Farm - General Toshevo). The system of belts in Dobrudja as a unique phenomenon in the agroforestry practice and an original ecology-biological phenomenon caused a great interest of participants (Snapshot 5). Everyone agreed that the forest belt system in Dobrudja is not only a national wealth, because of its uniqueness and the complex of benefits (services) it offers. This national wealth must be preserved, maintained and developed. It is necessary to develop PES schemes that provide funding for their sustainable management, as well as for the reconstruction and creation of new belts. The high professionalism and experience of Bulgarian foresters needs to be exported to Europe as a

good and successful practice that will greatly help to create protection belts in the other European countries and to find funds supporting the maintenance of Bulgarian shelter belts.

The biodiversity of wetlands in the Shabla and Balchik Municipalities as one of the main factors determine ecosystem sustainability in the context of climate change as well as the ecosystem services provided by wetlands were also discussed on the field trip.



Snapshot 5. Discussion on structure and benefits of forest belts.



Snapshot 6. Duranculak Lake and its biodiversity.



Snapshot 7. Longozes in Baltata Managed Reserve.



Snapshot 8. Archeological findings on B. Island

The protected area "Duranculak lake" (Snapshot 8), which is one of the most significant and best preserved coastal wetland in Bulgaria, registered under the Ramsar Convention and included in the Natura 2000 network was visited [6]. It is a natural liman fed by karst waters and separated from the Black sea by sand dunes and a beach strip. The Via Pontica road passes through and making it a suitable destination for ornithological tourism. Participants in the international meeting visited also the managed reserve "Baltata", located in close proximity to the Albena resort, where the northernmost longoz forests occupy a place (Snapshot 7). These forests are unique communities in the vegetation of Bulgaria with significant biodiversity and richness of conservation - significant species [7]. The forests are formed in the lower course of Batova River, which originates from the village of Kumanovo, the Frangen Plateau. The total length of Batova River is 39 km, the minimum run-off is 200-300 l / s. Longozes occurred at the end of the glacial period on quaternary deposits, rich, wet and deep soils. An important factor for their normal development is the soil moisture. The presence of evergreen and warm-loving species, as well as a more diverse species composition of tree layer, also a greater amount of wood and grass lianas distinguish these forests from the other riparian forests in Bulgaria (Regional Inspectorate of Environment and Water – Varna, Shabla Municipality, Green Educational Center). The managed reserve was commented on, as a natural example for the role of forests for the surface water purification.

There are 5 villages in the course of the river. The town of Balchik and v. Kranevo are resorts and Albena is a preferred resort on the seashore. They are located in the lower reaches of the river. During the summer season, the recreational load is strongly expressed. The agricultural lands also occupy a large area. Two roads from the State road network pass through the valley of the river. Extremely high pollution of the surface water flowing into the Batova river bed can be expected. According to the data from the national monitoring, the Batova River valley is characterized by medium to slightly polluted water and pure water flows into the sea. In this case, for the good ecological status of surface water in the Batova basin and coastal seawater, the regulating and supporting ecosystem services of longoze forests are of great importance. The maintained reserve "Baltata" also contributes significantly to the unique natural conditions that are offered to the visitors - a unique combination of preserved nature and a modern tourist resort providing various forms of recreation and ecotourism.

During the field trip, the rich cultural and historical heritage of Dobrudja and Durankulak as a complex archaeological site, where the highlights of Dobrudja's prehistory have been presented - an attractive center for the cultural and archaeological tourism [8-10]. The Big Island in Durankulak Lake and the Museum Collection in the Green Educational Center – Shabla were visited. On the Eneolithic settlement mound (Big Island), the oldest stone architecture in Europe (Dr. I. Weisssov, NAM, BAS) was found (Snapshot 8). The activities of Green Educational Center at Shabla Municipality for the environmental education is the most direct route for PES schemes realization and for sustainable development of region.

Cited sources:

[1] Payment for Ecosystem Services Cost Action/18.10.2016-17.10.2020 (CA 15206 PESFOR Forest for Water) <http://www.forestresearch.gov.uk/research/pesforw> .

[2] Contract DCOST 1/30/20.12.2017 – „Development of an ecosystem services assessment echeme, their effectiveness for purification and protection of water and other natural Components in the regions“ with National |Scientific Fund from Ministry of Education and Sciences to COST Action Payment for Ecosystem services (Forest for Water)/ CA 15206 PESFOR <http://www.e-ecology.org/esefas&forbel> .

[3] Tonev T., Nankova M., M. Stoyanova, 1995 - Influence of the protection belts in Dobroudja on the yield and quality of the bean. Plant Breeding Sciences, v. XXXII, No 5, 22-26.

[4] Tonev, T., M. Nankova, D. Georgiev, Iliev, G. Milev, P. Yankov, G. Sabev, N. Nankov, 2002. Strategy for the development of agriculture in Dobrich region since 2002. / ed.22.10.2004/.

[5] Tonev T. and I. Iliev, 2005. Distribution of the snow cover and the yield of wheat and maize grain in a sheltered field. Selection and Agrotechnics of Field Cultures, Part II, Balkan Scientific Conference - 2 June 2005, Karnobat, 380-384.

[6] Georgiev, D. Nature Spot "Durankulak Lake". Management Plan of БИШПОБ, Varna, 2001.

[7] Management Plan of the supported reservation "Baltata" Ord.№PД-1126/29.10., 2004.

[8] Orachev, A. Contributions to the paleogeography of the Dobroudja coast. - In: Sat. Dobrudja, 1990, vol. 7, 32-52.

[9] Todorova, H. Dobrudzha during the prehistoric age. - In: History of Dobrudja, vol I, S., 1984, 23-71.

[10] Todorova, H. et al. Durankulak, vol 1, C, 1989, 311 p.

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- Atanassova, I., S. Doerr, 2010. Organic compounds of different extractability in total solvent extracts from soils of contrasting water repellency. *European Journal of Soil Science*, 61, 298-313.
- Schwesig, D., A. Göttlein, L. Haumaier, R. Blasek, G. Ilgen, 2013. *International Journal of Environmental and Analytical Chemistry*. URL: <http://dx.doi.org/10.1080/03067319908032668>.
- Calderón, H. W., 1982. The content and composition of humus in arid alluvial soil of Peru. *Soil Science Academy of Sciences of USSR, Moscow*, 8, 53-59. (in Russian).
- Sparks, D. L., 2002. *Environmental Soil Chemistry*, 2nd Edition, Academic Press, San Diego, CA.
- Sparks, D. L., P.M. Huang, 1985. The physical chemistry of soil potassium. p. 201-276.
- In R.E. Munson (ed.) *Potassium in agriculture*. Soil Science Society of America, Madison, WI.
- Noyes, J. S., 2013. Universal Chalcidoidea Database. World Wide Web electronic publication. Last update 29 August 2013. URL: <http://www.nhm.ac.uk/chalcidoids>.

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